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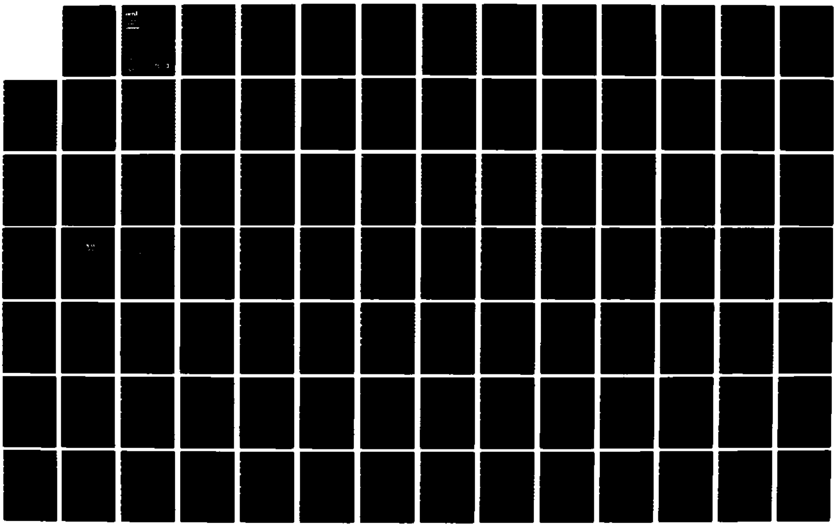

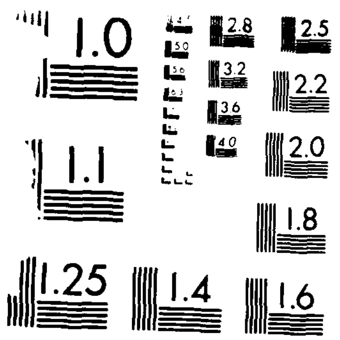

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DATABASE ASSESSMENT OF POLLUTION CONTROL IN THE MILITARY EXPLOSIVES AND PROPELLANTS PRODUCTION INDUSTRY

PREPARED BY

Bimal C. Pal
Michael G. Ryon

February 1986

SUPPORTED BY

U.S. ARMY MEDICAL RESEARCH
AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

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RDX	Pollution abatement	Army Ammunition Plants
HMX	Air Pollution	Manufacturing Processes
Nitroglycerin	Water Pollution	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A database on the current and proposed methods of pollution abatement in the munition production industry is presented. Information on current pollution status and waste treatment methods for the Army ammunition plants is also presented.

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DATABASE ASSESSMENT OF POLLUTION CONTROL IN THE MILITARY EXPLOSIVES AND PROPELLANTS PRODUCTION INDUSTRY

FINAL REPORT

Bimal C. Pal
Michael G. Ryon

Chemical Effects Information Task Group
Information Resources Organization
Oak Ridge National Laboratory
Oak Ridge, TN 37831

FEBRUARY 1986

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EXECUTIVE SUMMARY

The public concern for the protection of the environment against industrial pollution led to the promulgation of Executive Order 11597 dated February 1970 and later superseding orders which required all federal facilities to conform to federal environmental standards. Currently, the U.S. Army has 35 government-owned, contractor-operated (GOCO) plants located in 22 states. These facilities collectively represent one of the largest industrial manufacturing complexes in the United States and have now been placed under the jurisdiction of federal regulatory agencies such as the U.S. Environmental Protection Agency (USEPA) and the Occupational Health and Safety Agency and state pollution control boards. These developments provided the impetus to the Army to embark on an exemplary program to meet the regulatory constraints.

Two agencies were created and assigned to carry out the main task of modernization and pollution control in the Army Ammunition Plants (AAPs) -- the Production Base Modernization Agency and the U.S. Army Toxic and Hazardous Materials Agency. The former carries out the Manufacturing Methods and Technology Pollutant Abatement Technology Program (MMTPAT), and the latter is entrusted with the Pollution Abatement and Environmental Control Technology Program (PAECT). There is close collaboration between the two agencies to avoid any duplication of effort. The GOCO and GOGO (government-owned and government-operated) plants are heavily involved in both programs, and there is interaction with other government agencies and other establishments of the Department of Defense. The USEPA closely collaborates under the PAECT program. In 1985 and 1986, funding ($2.3 million) has been provided for developing sludge disposal technology, hydrogen peroxide treatment of Ammonia Oxidation Plant exhaust, assessment of technological advances for military unique pollutants, and pilot plant evaluation for treating detonator wastewaters at Kansas AAP under the MMTPAT program. A total of 20 different projects have been listed in the PAECT program. The areas emphasized ares: munition production wash treatment; recovery and reuse of munition wa tes; analysis of munition waste compounds; and treatment of nonmunition-related industrial pollutants.

The most modern, most highly automated, and highest capacity (50 tons/day) TNT manufacturing plant is the Radford AAP. Although the plant operates successfully, still several problem areas exist. The formation of the "white compound" (2,2'-dicarboxy-3,3',5,5'- tetranitroazoxybenzene), mainly in nitrator vessel No. 3, is a potentially dangerous occurrence. This formation can perhaps be minimized by changing the reaction parameters and by flushing the reaction mixture with nitrogen. Higher-than-expected consumption of raw materials is also a problem. About 35,000 lb/month of off-specification TNT is generated per continuous production line at Radford. Currently this material is incinerated. The possibility of recycling or upgrading this material is being investigated under the PAECT program. The emission of NO_x and tetranitromethane (TNM) from TNT manufacture has been considerably reduced after installation of a fume absorption system. However,

the emission of TNM is still a problem; currently it is vented to the atmosphere. The combination of nitric acid, sulfuric acid, and nitrosylsulfuric acid formed in fume scrubbing towers is highly corrosive to the material used in fabricating the equipment. Alloy 20 or Teflon-coated material is now being used.

Crude TNT as produced by the Radford process contains isomers that must be removed to prevent exudation. This has been achieved by the treatment of the crude TNT with sodium sulfite (sellite), which generates a large volume of wash water commonly known as red water. Radford AAP has been successful in disposing of red water to the paper industry. To provide a better solution to the problem, plans have been made to build a sulfite recovery plant based essentially on the Sonoco process.

Pink water, formed as a result of LAP (Load, Assemble and Pack) and other operations, is treated with carbon before discharge into natural streams. The explosive-laden carbon can be regenerated with 92 percent efficiency; but after four such cycles of regeneration, the carbon has to be discarded because of low adsorption efficiency. The spent carbon is usually incinerated.

The current trend in the AAPs is towards incineration and composting rather than open burning and land-filling for disposal of solid wastes containing energetic materials. A four million dollar rotary kiln incinerator facility has been successfully operated at Radford AAP. However, the capital and maintenance costs are high for this type of incinerator. Fluidized-bed incinerators using Al_2O_3 and NiO_2 (94:6 w/w) appear to be promising. Midland-Ross Corporation is developing an incineration facility with heat recovery. The Science Advisory Board of the USEPA has made the observation that, while the agency monitors what happens to specific chemicals being burned, many new chemicals and compounds formed and released in the incineration process are not monitored or analyzed.

A central biological wastewater treatment facility is operational at Radford AAP. The nitrate ester manufacturing wastewater is pretreated chemically prior to being combined with the propellant manufacturing wastewater for biological treatment. The biological treatment plant effluent has been found to be slightly more toxic to fish than the influent, presumably because of propellant ingredient interactions as well as chemical and biological transformations. This indicates the necessity of exercising extreme caution in composting explosive wastes. Many experts, including Dr. David L. Kaplan (U.S. Army Natick Research and Development Center), do not consider composting of TNT to be a viable option for the disposal of TNT wastes, because they have been unable to demonstrate the biodegradability of the aromatic ring of TNT. However, Atlantic Research Corporation is investigating the composting of TNT under the PAECT program. Both nitroglycerin and RDX are biodegradable; nitrocellulose is not. Many intermediates formed in the biodegradation of TNT and RDX have been identified. Biodegradability of HMX, SEX, and TAX has recently been demonstrated. Nitroguanidine is not susceptible to aerobic biodegradation in activated sludge; however, it can be cometabolized by anaerobic sludge microorganisms to nitrosoguanidine after acclimation. A report from Natick Laboratory indicates that nitroguanidine can be microbically degraded to ammonia in soil under continuous-flow microaerophilic conditions.

Sulfur dioxide emission arises from coal combustion and sulfuric acid production in the AAPs. The Electric Power Research Institute has recently published an excellent document on its abatement technology. The processes discussed include the interesting Japanese DOWA process, which involves absorption of sulfur dioxide in a solution of basic aluminum sulfate followed by oxidation and neutralization with limestone. There are eight operational DOWA systems in Japan.

Wastewaters associated with TNT production or LAP activities contain a wide variety of harmful pollutants prior to treatment. Pollutants from manufacturing TNT include TNT itself, other nitrobodies such as DNTs, NO_x, sulfates, elevated COD and BOD activity, increased levels of suspended and dissolved solids, and from dissolution of the stainless steel reaction vessels, increased levels of heavy metals such as chromium and copper. LAP activity wastewaters (pink water) contain similar pollutants except for the heavy metal concentrations. Most of these pollutants are reduced to acceptable levels after treatment with the state-of-the-art processes such as the ones at Radford AAP. Wastewaters associated with HMX and RDX contain the parent compounds, by-products SEX and TAX, suspended and dissolved solids, other nitrogen compounds, and heavy metals leached from production vessels. Treatment processes recently installed at Holston AAP have generally lowered the pollutant levels, but complete removal has not occurred and is probably unrealistic. Nitrocellulose production and LAP activity generate wastewaters with high levels of solids and nitrates. Nitroglycerin production wastewaters contain the parent compound as well as high levels of dissolved solids, total organic carbon, nitrate/nitrite levels, and COD activity.

Solid wastes from AAPs include spills of munition compounds or component chemicals, settling of airborne particles, ashes from incineration of wastes, spent activated carbon (used in wastewater treatment), and sludges from settling ponds and filtration devices. TNT production has been associated with high and sometimes persistent levels of TNT and by-products in soils and groundwaters located in the production areas of various AAPs. Ash analysis has shown that open burning of TNT waste often leaves significant amounts of TNT in the residual ash. A trend towards burning using fluidized beds or incinerators has been indicated because these processes leave less residual munitions. RDX and HMX solid wastes are similar to those of TNT, with the primary solid waste problem being the disposal of sludge from waste treatment facilities. The sludge consists primarily of ammonium nitrate and sodium nitrate with small amounts of explosives and other impurities. Groundwater surveys at Holston AAP have identified several pollutants of concern (e.g., dissolved solids), but no munition compounds or degradation products have been detected. However, recent soil analyses have indicated contamination. Sludge from centrifugation processes or other wastewater treatments are the main solid waste problem associated with nitrocellulose production. Studies of the fate of landfilled sludges indicated that nitrocellulose fines did not migrate, but nitrates/nitrites and cyanides did leach out. Sludges from nitroglycerin production are dominated by chemicals used for neutralization, and in surveys nitroglycerin has not been specifically identified in the sludge.

A brief review of the current pollution abatement status of the many AAPs (including LAP facilities) indicates that most of the operating plants have installed up-to-date treatment methods. These methods are based on research or pilot-plant activities performed at Radford and Holston AAPs. The AAPs on stand-by or inactive status usually fail to contain the appropriate treatment facilities to meet guidelines of the Resource Conservation and Recovery Act (RCRA) or other regulatory guidelines. Most of the facilities have had surveys to identify the steps needed to bring them into compliance, but actual work has been delayed by the inactive status. AAPs that do not handle munition compounds (either in production or LAP activities) are also identified. Most of these are involved in producing metal shell components or pyrotechnic charges.

An excellent book on the analysis of explosives has been recently published by Simon and Zitrin (Pergamon Press 1981). Analytical Methods for explosives and related materials have been described in the USEPA SW-846. For monitoring air pollutants, gas chromatography, thermo-electron analyzers, and infrared analyzers have been used, among other techniques. A groundwater sampling strategy and procedures for determining the reactivity of munition wastes need to be developed.

The USEPA has prescribed performance standards for new and modified sulfuric and nitric acid plants. Emission factors for several manufacturing processes such as sulfuric acid, nitric acid, and TNT manufacture have been given. Although the USEPA has not yet set any criteria for munition compounds in the effluent from the AAPs, interim environmental criteria for six munition compounds (nitrocellulose, white phosphorus, nitroglycerin, RDX, TNT, and 2,4-DNT) have been recommended by the U.S. Army Medical Research and Development Command following the methodologies proposed in the Federal Register by the USEPA. Guidelines have been published by the USEPA for the effluents from the munition plants concerning chemical oxygen demand, biological oxygen demand, total suspended solids, and pH.

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Preparation of this document would have been impossible without the active collaboration of personnel at several different Army installations. Thanks are due to Jesse J. Barkley, Jr., and Alan B. Rosencrance, Project Officers, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, Maryland, for their advice and for help in arranging site visits to Picatinny Arsenal (Dover, New Jersey), the U.S. Army Toxic and Hazardous Materials Agency (Aberdeen Proving Ground, Maryland), Holston AAP, and Radford AAP. At Dover, Joseph Taglairino, Morton Greene, Kit Wong, Jack Swotinsky, Jim Carrazza, and William Buckley, Jr., gave an overview of the work carried out at the Munition Production Base Modernization Agency. We also had an enlightening discussion of problems in the munition manufacturing industry with Everett E. Gilbert and Harold Matsuguma at Dover. We enjoyed the information and hospitality of Mike Mills, Johnny Evans, and Andrew F. Polahar, who showed us around Holston AAP. At Radford AAP, John Horvath, James A. Morris, Leonard L. Smith, William T. Bolleter, Lawrence Cali, and Carl D. Chandler generously shared their expertise in munition manufacture with us. We are much indebted to John Horvath for making the information on many ongoing projects at Radford available to us. David Renard and Charles Denzler furnished us with the details of the current program planning and operation of the U.S. Army Toxic and Hazardous Materials Agency. The authors are also greatly indebted to Lois Thurston, Carolyn Seaborn, and Jan Pruett for assistance in document preparation and collection and organization of reference materials.

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1. INTRODUCTION

Increased public awareness of environmental pollution during the late 1960s resulted in Executive Order 11597, dated February 1970, and later superseding orders which required all federal facilities to conform to federal environmental standards. During the period 1970 to 1977, expenditures in the environmental technology area were in excess of $27 million. Since then, an environmental technology program has been maintained at a level of $1 to $2 million annually. This financial support enabled the Army to launch an intensive program for pollution abatement in the Army Ammunition Plants (AAPs) (Zeigler 1980). A two-pronged attack has been developed to attain this objective: (1) to modernize and improve the existing technology of manufacture of ammunitions for increased efficiency of operation in order to cut down the extent of by-products and (2) to improve and/or develop technologies for handling the waste products. Considerable progress has been achieved by the Army in these two areas, and, as noted in this document, much remains to be done.

Since the U.S. Environmental Protection Agency (USEPA) report by Patterson et al. (1976), no comprehensive treatment of pollution control in the military explosives and propellants production industry has been issued. The latest volume (Volume 9) of the Encyclopedia of Explosives and Related Items (Kaye 1980) and Volume 4 of the Chemistry and Technology of Explosives (Urbanski 1984) partially address the subject. The main purpose of this document is to survey the literature of the past decade or so and present an up-to-date assessment of the status of pollution control in the AAPs.

To attain this objective, computerized searches were made on the databases of the Defense Technical Information Center (DTIC), the National Technical Information Service (NTIS), and MEDLARS, and on the commercially available database systems (e.g., DIALOG). Hardcopies of pertinent references were obtained and used in compiling the review. Site visits were made to Holston AAP, Radford AAP, the Production Base Modernization Activity and the Large Caliber Weapon Systems Laboratory at Dover, New Jersey, and the U.S. Army Toxic and Hazardous Material Agency at Aberdeen Proving Ground, Maryland, to gain first-hand experience of the munitions production industry and to gather the latest information on the ongoing projects in pollution abatement within the military explosives and propellants production industry. Personal contacts and discussion with the experts in this field have considerably enriched this review.

Section 2 deals with the physical and chemical properties of selected explosives, by-products, and related materials. Section 3 deals with the manufacture of the specific munitions. A scenario is presented in Section 4 to show the interaction among different agencies involved in the pollution abatement program. Actual and potential air pollution, water pollution, and solid wastes from the AAPs are covered in Sections 5 through 7. The current pollution and pollution abatement status of the various AAPs is discussed in

Section 8. Modernization, waste management, monitoring programs, and regulatory aspects are the respective subject matter of Sections 9 through 12. Data gaps and research needs identified as a result of literature analysis are discussed throughout the document. The general term TNT is used in this document to imply the specific isomer, α-trinitrotoluene.

2. PHYSICAL AND CHEMICAL PROPERTIES OF EXPLOSIVES AND RELATED MATERIALS

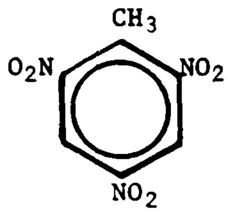
2.1 TNT

Data are from Lindner 1980, unless indicated otherwise.

Molecular formula: $C_7H_5N_3O_6$

Molecular weight: 227.13

Structural formula:



CAS registry number: 118-96-7

Chemical name: 2,4,6-Trinitrotoluene

Synonyms: TNT, 2-methyl-1,3,5-trinitrobenzene, α-trinitrotoluol, sym-trinitrotoluene, 1-methyl-2,4,6-trinitrobenzene, Tolit, Trilit, Trotyl, tritol, sym-trinitrotoluol (Windholz 1976)

Elemental analysis: C, 37.01 percent; H, 2.22 percent; N, 18.50 percent; O, 42.27 percent (Windholz 1976)

Melting point: 80.1°C (Windholz 1976); 80.8°C, pure; >80.2°C, military grade (Urbanski 1984)

Boiling point: 190°C/2 mm Hg, 245-250°C/50 mm Hg (Urbanski 1983b)

Density: D_4^{20} 1.654 (solid) (Windholz 1976); 1.467 at 82°C (Urbanski 1983b)

$d(g/cm^3) = 1.5446 - 1.016 \times 10^{-3}t$, where t = °C; applicable in the temperature range 83°-120°C

Dipole moment: 1.37D (Windholz 1976)

Hygroscopicity: Nonhygroscopic

Vapor pressure: 0.046 mm Hg at 82°C (TDB 1982)

Stability: TNT is very stable and may be stored indefinitely at temperate conditions without deterioration.

Decomposition: The decomposition mechanism of TNT at elevated temperatures (200°C) is very complex, producing at least 25 different compounds as well as large amounts of undefined polymeric material.

Viscosity: 8 cP at 99°C

Detonation products (experimentally determined in a calorimetric bomb, mole per mole TNT): 3.65 C (sol), 1.98 CO, 1.60 H_2O, 1.32 N_2, 0.46 H_2, 0.16 NH_3, and 0.10 CH_4

Heat of formation, kJ/g: 0.293

Heat of combustion, kJ/g: 15.02

Heat of detonation, kJ/g: 4.23

Specific heat, J/(g·K): 1.38

Heat of fusion, J/g: 98.3

Heat of vaporization, J/g: 339

Heat of sublimation, J/g: 447

Thermal conductivity, W/(m·K): 0.54

Coefficient of linear expansion: 6.7×10^{-3}/°C

Solubility (g/100 g) at 20°C (Windholz 1976):
Water: 0.01
Other solvents: pyridine - 137; acetone - 109; methyl acetate - 7211; benzene - 67; toluene - 55; chlorobenzene - 33.9; chloroform - 19; 1,2-dichloroethane - 18.7; diethyl ether - 3.29; trichloromethylene - 3.04; 95 percent ethanol - 1.23; carbon tetrachloride - 0.65; carbon disulfide - 0.48

TABLE 2.1. SPECIFICATIONS FOR TWO MILITARY GRADES OF TNT IN THE UNITED STATES[a]

Property	General Type I	Special Type II[b]
Solidification point (°C-min)	80.2	80.4
Moisture (% max)	0.10	0.10
Acidity (as H_2SO_4 % max)	0.02	0.02
Alkalinity	None	None
Insoluble matter, (% max)	0.05	0.05
Sodium, (% max)	0.001	0.001
Color	Light yellow through buff	Light yellow

a. Adapted from Gilbert (1980).

b. Urbanski (1983a) lists the melting point of Grade II (USA) TNT as 76.0°C.

USSR standards specify the following grades of TNT (Urbanski 1983b):

Military TNT - melting point (m.p.) 80.2°C

TNT for the manufacture of ammonites -

(a) Sulfited (for permissible explosives) m.p. 80.2°C
(b) Washed only m.p. 77.5°C

Waste TNT - m.p. 75°C

TABLE 2.2. EUTECTICS WITH TNT[a]

The Second Component	Weight % of TNT	Melting Point (°C)
Cyclonite	97.5	78.6
m-Dinitrobenzene	54.5	51
1,8-Dinitronaphthalene	82	73.4
	46	45
	48	45.8
	47.4	46.3
Hexyl	88	78.2
Nitrobenzene	7	2.0
Nitroglycerin	17.6	7.0
	15	6.4
	17.1	6.3
o-Nitrotoluene	16	-15.6
	19.5	-9.7
p-Nitrotoluene	42	34
Pentaerythritol tetranitrate	87	76.1
Picric acid	65	59.8
	66	55
	68	59
	66.4	63.3
Tetryl	57.9	58.3
Trinitro-m-cresol	43.3	41.3
Trinitro-m-xylene	92	75

a. Adapted from Urbanski (1983b).

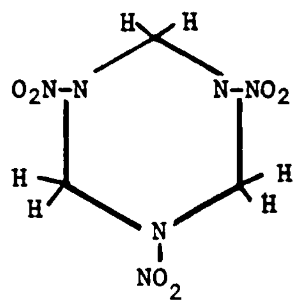
2.2 RDX

Data are from Lindner (1980), unless indicated otherwise.

Molecular formula: $C_3H_6N_6O_6$

Molecular weight: 222.13

Structural formula:



CAS registry number: 121-82-4

Chemical name: Hexahydro-1,3,5-trinitro-1,3,5-triazine

Synonyms: RDX (British code name for Research Department Explosive or Royal Demolition Explosive, cyclotrimethylene trinitramine, cyclonite, hexogen, PBX (AF) 108, T4, 1,3,5-triaza-1,3,5-trinitrocyclohexane, trimethylenetrinitramine, 1,3,5-trinitroperhydro-1,3,5-triazine

Elemental analysis: C, 16.22 percent; H, 2.72 percent; N, 37.83 percent; O, 43.22 percent

Color: White

Crystal density, g/cm^3: 1.83

Crystal form: Orthorhombic

Melting point: 204°C

Hardness, Mohs: 2.5

Oxygen balance, percent to CO_2: -22

Heat of formation, kJ/g: -0.277

Heat of fusion at 478.5 K: 8.5 kcal/mole (Roth 1980)

Heat of combustion, kJ/g: 9.46

Specific heat, J(g·K): 1.26; 0.398 cal/g°C at 20°C (Roth 1980)

Heat of vaporization, J/g: 490

Heat of sublimation, kcal/mole: 31.1 (Roth 1980)

Detonation products (calculated values, mole per mole RDX): 3.00 N_2, 3.00 H_2O, 1.49 CO_2, and 0.02 CO

Stability: Stored at 85°C for 10 months without perceptible deterioration

Dipole moment: ~7D (in highly polar solvents) (Roth 1980)

Solubility: water at 25°C, 7.6 mg/L; water at 83°C 1.3 g/L; acetone at 30°C, 69.0 g/L; cyclohexanone at 30°C, 84.0 g/L; acetic anhydride at 30°C, 49.0 g/L (Patterson et al. 1976)

TABLE 2.3. VARIATION IN SOLUBILITY OF RDX WITH TEMPERATURE AND SOLVENT[a]

Solvent	25°C	40°C	60°C	80°C	98°C
Dimethyl sulfoxide	41[b]	51	66	87	113
Dimethyl formamide	37	45	58	76	96
N-Methylpyrrolidone	40	47	58	72	84
Butyrolactone	14	-	29	41	61
Acetone	8.2	12	17 (56.5°C)	-	

a. Adapted from Gilbert (1980).

b. Values in g RDX per 100 g solvent.

Ultraviolet absorption spectrum: λmax, 202 nm; shoulder, 236 nm (in ethanol) (Urbanski 1984)

Specifications for RDX (USA)-Specification of 1963 cover two types of RDX (Urbanski 1984)

Type A - Made by the nitric acid method

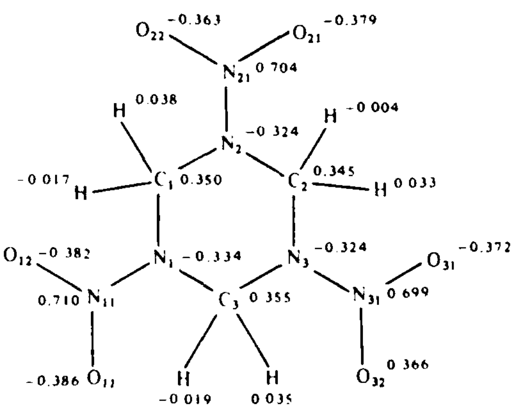
Type B - Made by the acetic anhydride process

TABLE 2.4. PROPERTIES OF TYPE A AND TYPE B RDX

Property	Type A	Type B
Melting point	200°C	190°C
Acetone insoluble (max)	0.05%	0.05%
Inorganic insoluble (max)	0.03%	0.03%
Particles retained on U.S. Standard Sieve No. 60 (max)	5	5
Acidity (max)	0.05% as HNO_3	0.02% as CH_3COOH

Electron density of RDX:

ORNL-DWG 86-7593



CYCLONITE (HEXOGEN, RDX) (URBANSKI 1984)

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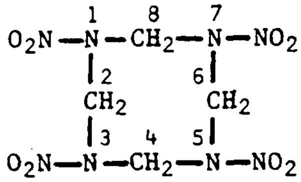
2.3 HMX

Data are from Lindner (1980), unless indicated otherwise.

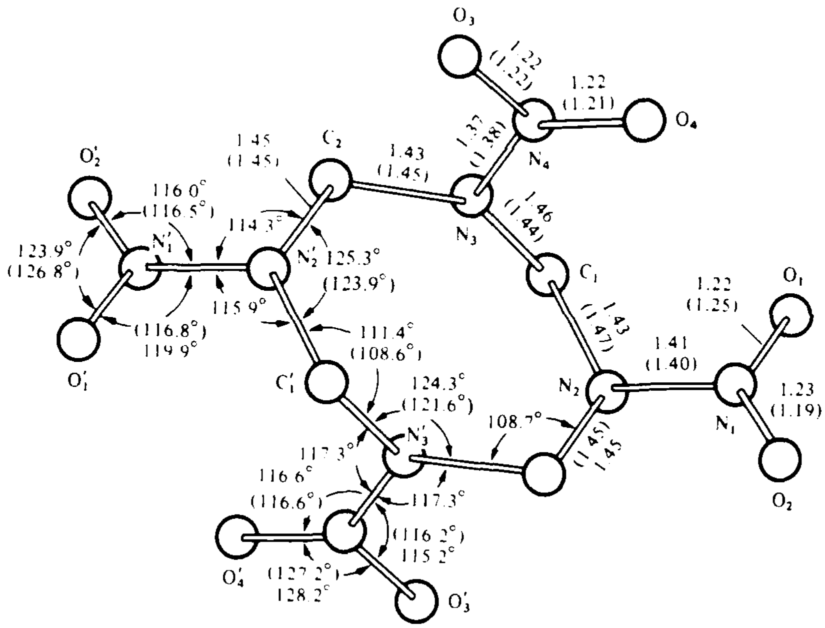
Molecular formula: $C_4H_8N_8O_8$

Molecular weight: 296.17

Structural formula:



ORNL–DWG 85-9461



Structure of β-Octogen. Data from ESR (Electron Spin Resonance) are bracketed. (Urbanski 1984) Reprinted with permission of Pergamon Press and author.

CAS registry no.: 2691-41-0

Chemical name: Cyclotetramethylenetetranitramine

Synonyms: HMX (High Melting Explosive, Fedoroff and Sheffield 1966a), β-HMX homocyclonite, HW4, LX 14-0, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, octogen, tetramethylenetetranitramine, 1,3,5,7-tetraza-1,3,5,7-tetranitrocyclooctane

Elemental analysis: C, 16.22 percent; H, 2.72 percent; N, 37.84 percent; O, 43.22 percent

Color: White

Crystal density, g/cm^3: 1.90 (beta)

Crystal form: Four polymorphic forms, beta-form least sensitive and most stable

TABLE 2.5. SOME PROPERTIES OF HMX MODIFICATIONS[a]

Property	β	α	γ	δ
Region of stability	Room temperature to 115°C	115-156°C	156°C	156-281.5°C
Melting points (on rapid heating)	246-247°C	256-257°C	278-280°C	280-281.5°C
Molar refraction[b]	56.1	55.7	55.4	55.9
Sensitivity to impact mass in kg/height	5/15	1/20	1/20	1/10
energy of impact kg/cm^2	0.75	0.2	2.2	0.1

a. Adapted from Urbanski (1984).

b. Values in table are measured, the calculated value is 58.

TABLE 2.6. VARIATION IN SOLUBILITY OF HMX WITH TEMPERATURE AND SOLVENT[a]

Solvent	25°C	60°C	98°C
Dimethylsulfoxide	57[b]	68	89
Dimethylformamide	Solvate[c]	Solvate	Solvate
N-Methylpyrrolidone	Solvate	Solvate	Solvate
Butyrolactone	12	20	35
Acetone	2.8	4.2[d]	-
Butyrolactone (73%) dimethylsulfoxide (27%)	26	33	49

a. Adapted from Kaye (1980b).

b. Grams of HMX per 100g of solvent, after 5 mins of stirring.

c. Shortly after the HMX dissolves, precipitation of the solvate crystals occurs.

d. At the boiling point.

Melting point: 286°C

Hardness, Mohs: 2.3

Solubility, g/L: Water at 83°C - 0.14; acetone at 30°C - 22.0; cyclohexanone at 30°C - 53.0; acetic anhydride at 30°C - 13.0 (Patterson et al. 1976)

Oxygen balance, percent to CO_2: -22

Heat of formation, kJ/g: -0.253

Heat of combustion, kJ/g: 9.43

Heat of detonation, kJ/g: 5.67

Specific heat, J(g·K): 1.26

Heat of vaporization, J/g: 368

Detonation products (experimentally determined in a calorimetric bomb, mole per mole HMX):
$3.68\ N_2$; $3.18\ H_2$; $1.92\ CO_2$;
$1.06\ CO$; $0.97\ C$, $0.395\ NH_3$; $0.30\ H_2$

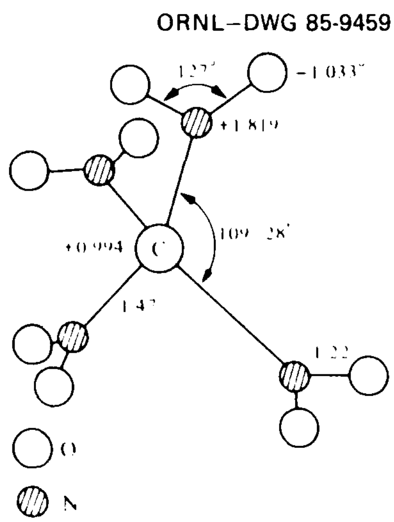
2.4 TETRANITROMETHANE

Data are from Clayton and Clayton (1982), unless indicated otherwise.

Molecular formula: $C(NO_2)_4$

Molecular weight: 196.04

Structural formula: (Urbanski 1984)



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CAS registry no.: 509-14-8

Chemical name: Tetranitromethane

Synonyms: Tetranitromethan (German), Tetranitromethano (Italian), Tetranitromethan (Russian) (McDonnell 1978)

Elemental Analysis: C, 6.13 percent; N, 28.58 percent; O, 65.29 percent

Melting point: 14.2°C

Boiling point: 125.7°C

Density: 1.62294/25°C

Refractive index: 1.43822 (McDonnell 1978)

Solubility: Insoluble in water at 20°C

Vapor pressure: ~13 mm Hg/25°C, 8.4 torr/20°C (11,000 ppm or 90,000 mg/m^3)

Vapor density: 0.8 (air = 1)

Assay: Collection in reagent grade methanol followed by reading at 240 nm and comparison with standard calibration curves using mass spectrometry, gas chromatography, or infrared analysis.

Color: Colorless, but becomes yellow on contact with water due to hydrolysis to trinitromethane.

Odor: Distinct pungent odor (characteristic acrid biting odor)

Physical state: oily fluid

Explosion temperature: Does not explode below 360°C (McDonnell 1978).

Heat of combustion: 102.9 kcal/mole (McDonnell 1978)

Heat of explosion (Qe): From differential thermal analyses, exothermic at 310°C; the Qe at 227°C was calculated to be 557 cal/g (McDonnell 1978)

Heat of formation: -8.9 kcal/mole (McDonnell 1978)

Spectrum, ultraviolet: λ_{max}, ~275 nm; log ε, 2.2 (McDonnell 1978)

Spectrum, infrared: Two strong bands at 1618 and 1266 cm^{-1} corresponding to asymmetric and symmetric vibrations, respectively, and a number of less prominent bands at 1645, 1439, 1370, 990, and 973 cm^{-1} (Urbanski 1984)

Transition point between the two crystalline forms: -99.8°C (from examination of the infrared spectra of TNM at different temperatures, -40°C to -126°C) (Urbanski 1984)

Energy of formation: 4.7-8.9 kcal/mol (Urbanski 1984)

Enthalpy of formation: -18.5 kcal/mol (Urbanski 1984)

Heat of decomposition: $C(NO_2)_4 \rightarrow CO_2 + 3O_2 + 2N_2$ + 89.6-102.9 kcal/mol (Urbanski 1984)

Charge transfer complexes: Forms characteristic charge transfer complexes with unsaturated compounds (Urbanski 1984)

Reaction with sulfites: $C(NO_2)_4 + Na_2SO_3 \rightarrow (O_2N)_3CSO_3Na + NaNO_2$ (Urbanski 1983b)

Thermal stability: At 100°C it evolves acid fumes in 30 min; at 135°C there is no explosion after 300 min (McDonnell 1978).

Formation from TNT: By the use of ^{14}C-labeled TNT, it was shown that 54.2 percent of the tetranitromethane came from the aromatic C attached to the methyl group, 8.3 percent from each of the C atoms connected to nitro groups, 7.4 percent from each of the C atoms attached to H, and 6.1 percent from the methyl group (McConnell 1978).

2.5 TRINITROMETHANE

Data are from McDonnell (1978), unless indicated otherwise.

Synonyms: Nitroform (German), Nitroforme (French)

CAS registry no.: 517-25-9

Molecular formula: $CH(NO_2)_3$

Structural formula:

$$(O_2N)_3\text{-CH} \longleftrightarrow (O_2N)_2C = NOOH$$

Nitro-form   Aci-form

(Urbanski 1983c)

Molecular weight: 151.04

Melting point: 26.3 ± 0.1, higher melting form (aci-form) melts at 50°C

Boiling point: 45-47°C/22 mm Hg

Density: 1.5967 at 24.3°C

Explosion hazard: Explodes when heated rapidly; can explode during distillation

Physical state: Colorless to pale yellow solid

Refractive index: 1.44174 at 24.3°C

Acidity: The pH of a saturated aqueous solution, 0.6

Spectrum, ultraviolet: Shows a plain shoulder in ethanol, and in water shows a broad maximum at 340 nm

Stability: May be stored indefinitely at 0°C in sealed glass ampoules

Chemical reactions: Trinitromethane is a strong acid and forms salts with metals and organic bases; it forms complexes with benzene and toluene

2.6 METHYL NITRATE

Data are from Clayton and Clayton (1982).

Molecular formula: CH_3NO_3

Structural formula: CH_3ONO_2

Molecular weight: 77.042

Boiling point: 65°C (explodes)

Specific gravity: 1.217 (15°C)

Vapor density: 2.66 (air = 1)

Solubility: Slightly soluble in water, soluble in alcohol and ether

2.7 SEX

Data are from Fedoroff et al. (1960b), unless indicated otherwise.

Chemical name: 1-Acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine

Synonyms: QDX, 1-acetyl-3,5,7-trinitro-octahydro-s-triazine, octahydro-1-acetyl-3,5,7-trinitro-s-tetrazocine

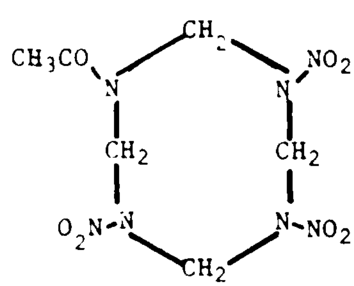
CAS registry no.: 13980-00-2

Molecular formula: $C_6H_{11}N_7O_7$

Elemental analysis: C, 24.58 percent; H, 3.78 percent; N, 33.44 percent; O, 38.20 percent

Molecular weight: 293.208

Structural formula:



Melting point: 224.2-224.7°C with frothing

Solubility: Slightly soluble in pyridine, acetone, and nitromethane; nearly insoluble in alcohol, benzene, acetic acid, and ether

Ultraviolet spectrophotometric data: λ_{max}, 227 nm; ε_{max}, 15,800 (Schroeder et al. 1951)

2.8 TAX

Data are from Fedoroff et al. (1960b), unless indicated otherwise.

Chemical name: 1-Acetylhexahydro-3,5-dinitro-1,3,5-triazine

CAS registry no.: 14168-42-4

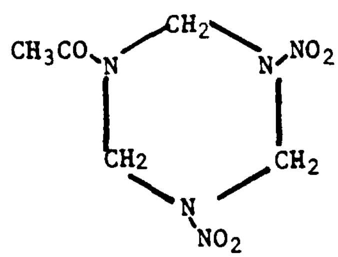
Synonyms: 1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane, 1-acetyl-3,5-dinitro-s-triazine, 1,5-dinitro-3-acetyl-1,3,5-triazine

Molecular weight: 219.162

Molecular formula: $C_5H_9N_5O_5$

Elemental analysis: C, 27.4 percent; H, 4.14 percent; N, 31.96 percent; O, 36.50 percent

Structural formula:



Melting point: 156-158°C

Solubility: Soluble in acetone, alcohol

Ultraviolet spectrophotometric data: λ_{max} 231-234 nm, ε_{max} 6500 (Schroeder et al. 1951)

2.9 CELLULOSE NITRATE/or NITROCELLULOSE

Data are from Fedoroff and Sheffield (1962a), unless indicated otherwise.

General formula: $C_6H_7(OH)_x(ONO_2)_y$, where X + Y = 3

Percentage composition: A product containing one NO_3 grouping per C_6 will contain 6.76% N, two NO_3 groupings 11.1% N, and three NO_3 groupings 14.14%.

$Y = \frac{162N}{1400-45N}$, where Y is the number of NO_3 groupings per C_6 and N is the nitrogen percentage of the product.

TABLE 2.7. MILITARY GRADES OF NITROCELLULOSE (NC)

	Nitrocellulose	Nitrogen Content (%)
Grade A	Pyrocellulose	
Type I		12.60 ± 0.10
Type II		12.60 ± 0.15
Grade B	Gun cotton	>13.35
Grade C	Blend	
Type I		13.15 ± 0.05
Type II		13.25 ± 0.05
Grade D	Pyroxylin	12.20 ± 0.10
Grade E		12.00 ± 0.10

TABLE 2.8. SPECIFIC GRAVITY OF NITROCELLULOSE

Nitrogen Content	Specific Gravity at 15°C	
	in xylene	in water
11.61	1.666	1.655
11.73	1.622	1.655
12.20	1.630	1.655

TABLE 2.9 SOLUBILITY OF NITROCELLULOSE IN ETHER-ALCOHOL[a]

Water Content of Nitrating Acid (%)	Nitrogen Content of Nitrocellulose (%)	Solubility (%)	Molecular Weight of Nitrocellulose (from Viscosity Measurements)
3.73	13.34	1.81	220,000
5.12	13.38	3.76	150,000
6.99	13.43	3.51	170,000
12.92	13.33	3.12	190,000
13.77	13.40	3.67	185,000
15.61	12.62	89.00	150,000
15.87	12.72	100.00	130,000
18.60	11.81	100.00	90,000
18.76	11.94	100.00	95,000
21.50	10.03	36.21	40,000
22.33	9.64	28.25	25,000

a. At 4-3 wt/wt.

Solubility: Solubility depends on (1) the degree of polymerization and (2) the nitrogen content of nitrocellulose (Urbanski 1983c).

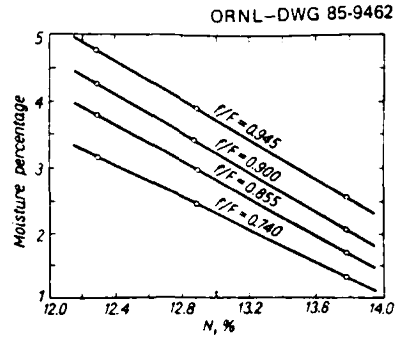
Ultraviolet absorption spectra: λmax, ~ 220 nm; ε = 15.0 for nitrocelluloses having a range of nitrogen contents from 10.9 to 14.1% (Urbanski 1983c)

Heat of absorption (Urbanski 1983c):

Nitrocellulose, 14% N:	ethanol	1.30 kcal/mole solvent
	ether	2.50 kcal/mole solvent
	acetone	3.88 kcal/mole solvent
Nitrocellulose, 11.5%N:	ethanol	1.80 kcal/mole solvent
	ether	3.37 kcal/mole solvent
	acetone	4.09 kcal/mole solvent

Heat of formation: 523.4-525.4 cal/g of cellulose trinitrate (Urbanski 1984)

Hydroscopicity:



Hygroscopicity of nitrocellulose as a function of nitrogen content at different relative humidities (Urbanski 1983c).
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2.10 NITROGUANIDINE

Data are from Carrazza (1983)

Molecular formula: $CH_4N_4O_2$

Structural formula: $H_2NC(=N-NO_2)NH_2$ (Form A),
$H_2NC(=NH)NHNO_2$ (Form B)

CAS registry number: 556-88-7

Molecular weight: 104.074

Appearance: Colorless crystals

Melting point: 232°C (decomposes)

Density: 1.72g/cm^3

Vapor pressure: Extremely low

Heat of combustion: 209 kcal/mole

Stability: Sensitive to ultraviolet radiation, absorbs at 264 nm; explosive when subjected to shock or exposed to heat or flame.

Solubility: Water - 4.4 g/L at 25°C; 83.5 g/L, at 100°C
Base (1 N KOH) - 12 g/L at 25°C
Acid (40 percent H_2SO_4) - 80 g/L at 25°C

2.11 GLYCEROL TRINITRATE/NITROGLYCERIN

Data are from Fedoroff and Sheffield (1972b), unless indicated otherwise.

Molecular Formula: $C_3H_5N_3O_9$

Molecular Weight: 227.09

Structural formula:

$$
\begin{array}{l}
CH_2ONO_2 \\
| \\
CHONO_2 \\
| \\
CH_2ONO_2
\end{array}
$$

CAS registry number: 55-63-0

Chemical name: 1,2,3-Propanetriol trinitrate

Synonyms: Nitroglycèrine (French), Nitroglyzerine (German) Nitroglycerina (Italian, Spanish), Nitroguriserin (Japanese), Nitroglytserin (Russian)

Elemental analysis: C, 15.87 percent; H, 2.22 percent; N, 18.50 percent; O, 63.41 percent.

Physical appearance, odor, and taste: Clear, colorless, odorless, oily liquid having a sweet burning taste

Specific gravity: 1.591 at 25°C

Refractive index: 1.4713 at 25°C

Freezing point: 13.2°C (stable form), 2.2° (labile form)

Boiling point: 145-150°C (decomposes); 125°C/2 mm Hg and 180°C/50 mm Hg (Fedoroff and Sheffield 1974b)

Hygroscopicity: 0.06% at 30°C and 90% relative humidity

Specific heat: 0.356 cal/g/°C for liquid, 0.315 cal/g/°C for solid

Viscosity: 36.0 centipoise at 20°C

Vapor pressure (°C, mm Hg): 15, 0.00130; 25, 0.00177; 35, 0.00459; 45, 0.01294; 55, 0.03587 (decomposition begins at 50-60°C) (Fedoroff and Sheffield 1974b)

Solubility: In water - 1.8 g/L (20°C); 2.5 g/L (50°C)
In ethanol - 37.5g/100g (0°C); 54g/100g (20°C); 40g/100g in 96 percent ethanol (20°C)
In carbon disulfide ~ 1.25g/10 mL (room temperature)
In miscellaneous solvents - 2 mL/10 mL carbon tetrachloride; 20 percent in trichloroethylene (Fedoroff and Sheffield 1974b)

Completely miscible in all proportions with methanol, ethyl acetate, acetic acid, benzene, toluene, xylene, phenol, nitrobenzene, nitrotoluene, pyridine, chloroform, dichloroethane, dichloroethylene, and the like. (Urbanski 1983c)

Surface tension at any temperature, T (K): γ(dynes/cm) = 94.58 [(720-T)/720] (Fedoroff and Sheffield 1974b)

Heat of combustion: 1616 cal/g

Heat of detonation: 1486 cal/g

Heat of explosion: 1600 cal/g

Heat of formation: 400 cal/g

Heat of evaporation (kcal/mole): 20.64 (100 K), 20.38 (140 K), 20.11 (180 K) (Urbanski 1983c)

Heat of crystallization: 33.2 cal/g (stable form), 5.2 cal/g (labile form)

3. MANUFACTURE OF EXPLOSIVES AND RELATED MATERIALS

A comprehensive treatment of the manufacture of explosives and propellants is beyond the scope of this document. For this, the reader may consult the standard treatises such as the Encyclopedia of Explosives and Related Materials, Vols. 1 to 10 (Fedoroff et al. 1960a; Federoff and Sheffield 1962b, 1966b, 1969, 1972a, 1974a; Fedoroff et al. 1975; Kaye 1978, 1980a, 1983), published by the Picatinny Arsenal, Dover, New Jersey, and the Chemistry and Technology of Explosives, Vols. 1 to 4 (Urbanski 1983a, 1983c, 1983e, 1984). In this section are outlined the current manufacturing methods, as adopted in modernized AAPs, with emphasis on by-products. The discussion in this section has been limited to explosives, propellants, and related materials of major significance.

3.1 MANUFACTURE OF TNT

TNT has been traditionally manufactured by nitration of toluene in several stages by using a mixture of H_2SO_4 and HNO_3 as the nitrating agent. Over the years many improvements in the manufacture of TNT and its purification have taken place but the basic principle has not changed (Urbanski 1983a).

A major improvement in the commercial manufacture of TNT took place when the continuous method of manufacture replaced the batch process (Urbanski 1983b). The British method of continuous manufacture of TNT was developed in the Oldbury plant, which came into operation in 1917. During World War II a continuous method developed by J. Meissner was introduced at the Schlebusch factory in Germany. A 1953 study group concluded after a survey of the seven known European continuous processes that the Bofors-Norell process was the best (Gilbert 1980, citing data of Wendes and Little 1954). This process includes both continuous nitration of toluene or mononitrotoluene to trinitrotoluene and continuous crystallization of the product (TNT) from dilute nitric acid (Urbanski 1983b). A second study group in 1967 selected the Swedish Nobel-Chematur Process as modified by Canadian Industry Ltd. (using sodium sulfite instead of nitric acid in the purification step) as the best available continuous process (Gilbert 1980, citing data of Slemrod 1970). A further modification of this process that became the first continuous method of TNT manufacture in the United States in 1968 at the Radford AAP.

The modern continuous process has several advantages over the batch process of manufacture of TNT (Urbanski 1983a):

1.) A much smaller quantity of explosive accumulates at any moment in the plant. According to A. B. Bofors, a plant with a daily production of 7.5 tons of TNT by the batch process, will accumulate at any moment 10 tons of explosive with a volume of approximately 50 m^3, compared to 4 tons and 12 m^3, respectively, for a plant with twice this capacity using the continuous process;

2.) Plant automation features such as flow regulators and temperature control offer a much higher degree of safety, a factor of paramount importance in explosive manufacture; and

3.) A relatively smaller plant and labor force is required for the same output of TNT.

The three continuous production lines of TNT at Radford have been a showpiece among all the AAPs. One of the lines was, however, lost in an accident in 1974 (Gilbert 1980). Although the design of this installation was based upon that of a plant already in successful operation, the Radford unit was double the size of the prototype, which necessitated the projection of scale-up factors. As a result, a year of trial and error operation was required before stable, steady-state operation was achieved yielding specification-grade TNT. However, there were still some problem areas, such as the higher-than-expected consumption of raw materials (e.g., Table 3.1). This problem was solved at Radford AAP by modifying the production process (see discussion below and Figure 3.2 and 3.3) (Bolleter 1985). The new process was computer-simulated and a computer-based system permitting more precise and remote process control was devised. On-line analyzers avoided the need for sample retrieval and provided the process control (Gilbert 1980).

In the original Radford process, 99 percent nitric acid and 40 percent oleum are introduced countercurrent to the nitrobody in a series of six stages, the temperature and compositions of which are given in Table 3.2 (Gilbert 1980).

Each stage includes a 500-gallon nitrator and a gravity separator for producing 50 tons of TNT per day. The purification section consists of an acid washer, two sellite washers, and a post-sellite washer (Figure 3.1). This process is still operational at Volunteer AAP, Newport AAP, and Joliet AAP (Bolleter 1985).

It was realized during the investigation of the 1974 accident at Radford AAP that acid-nitrobody emulsions can be explosive. To ensure safety and efficiency of operation, the newly modified Radford process employs eight nitrator vessels fitted with dynamic (centrifugal) separators (Figures 3.2 and 3.3), which are much more efficient than previously used gravity separators. The purification section utilizes two acid washes, three sellite washers, and two post-sellite washers (Bolleter 1977). This change resulted in a cleaner separation of the acid and nitrobody phases and in a drastic reduction of the total quantity of nitrobody present in the building at one time, 40 to 50 percent of that present with the use of gravity separators.

The yield losses <u>based</u> <u>on</u> <u>toluene</u> for the manufacture of TNT at the Radford AAP areas are (in percentage):

Meta TNT isomer formation	4
Methyl group oxidation	2-3
Oxidative cleavage of ring	7-8
During purification	2-3
Total	15-18

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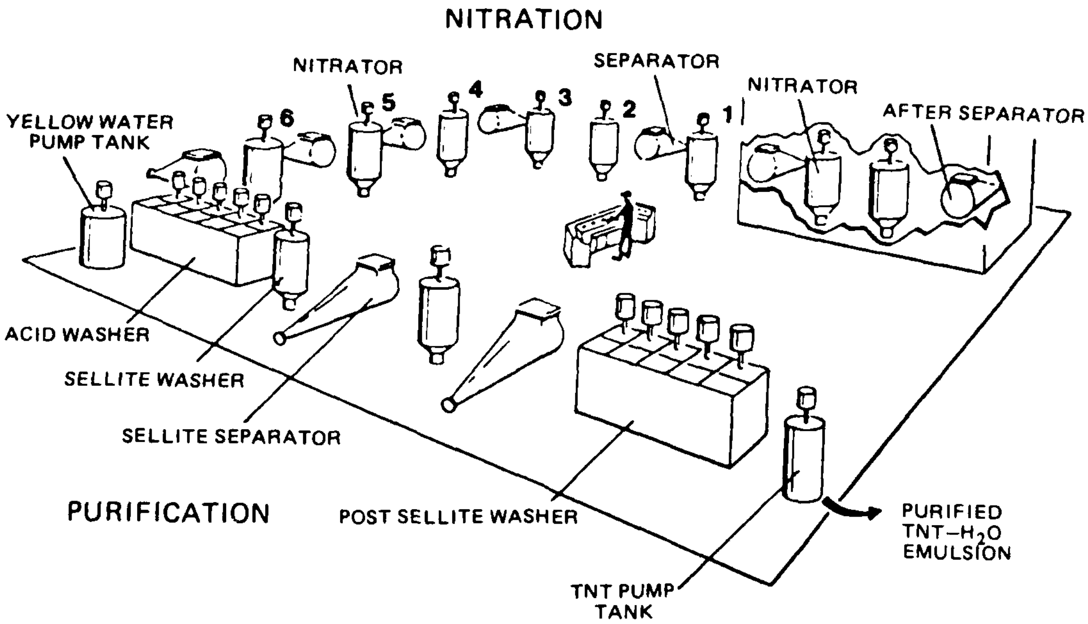

Figure 3.1. TNT nitration and purification equipment arrangement in the original Radford process. Adapted from Bolleter 1977.

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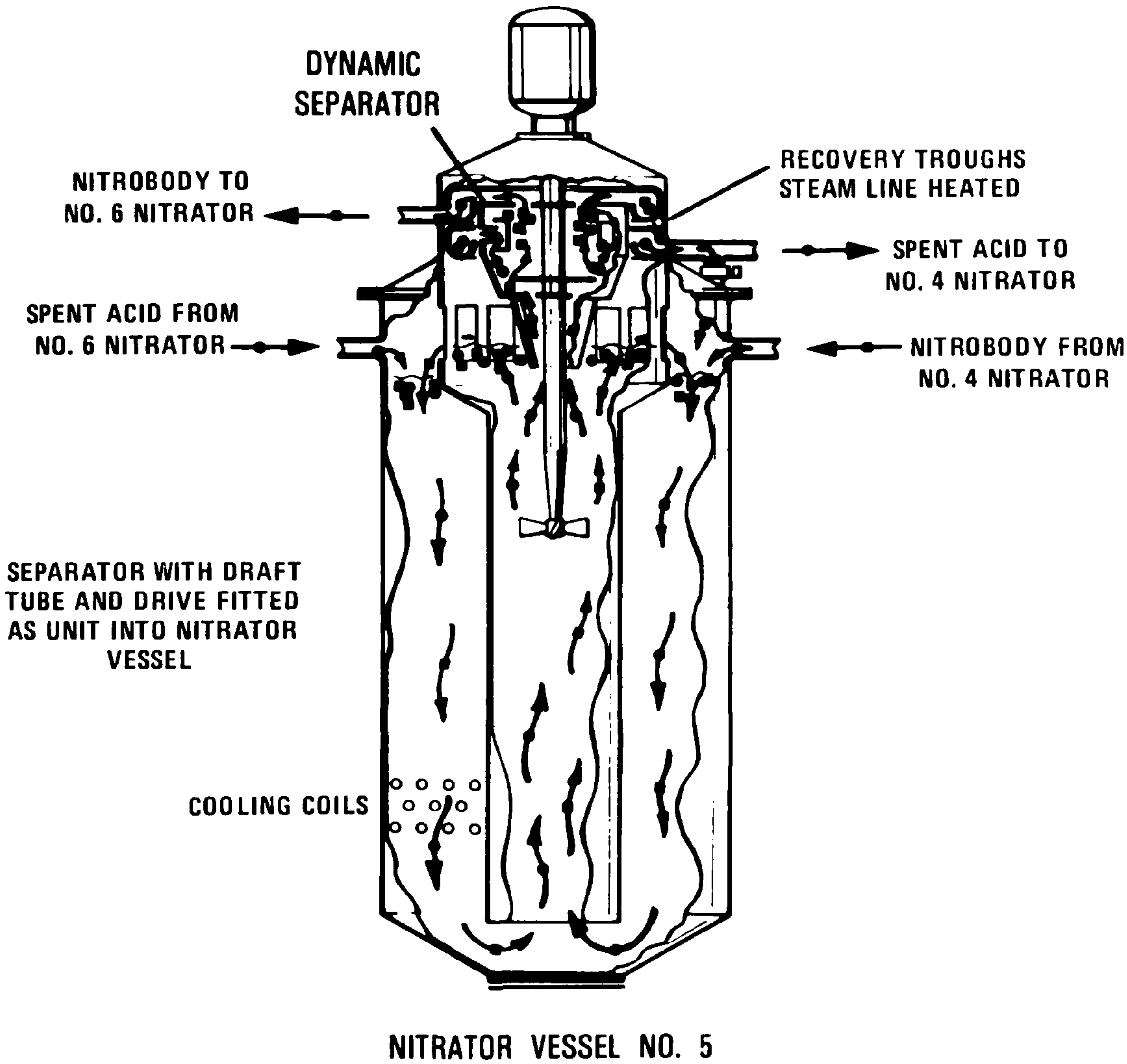

Figure 3.2. Nitrator with dynamic separator. Adapted from Gilbert 1980.

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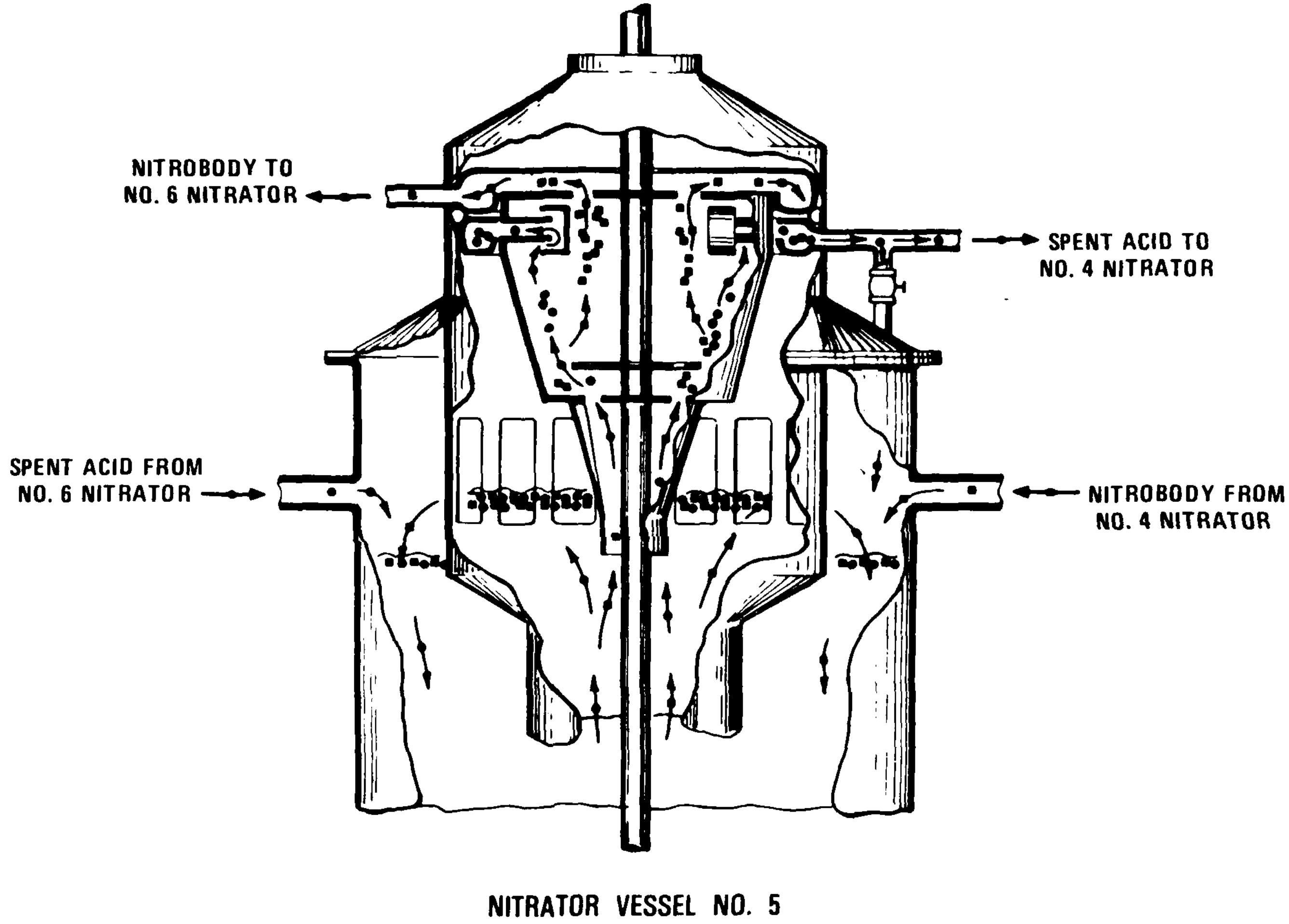

Figure 3.3. Dynamic separator. Adapted from Gilbert 1980.

TABLE 3.1. RAW MATERIALS CONSUMPTION FACTORS FOR A TYPICAL PRODUCTION LINE[a]

Material	Design	Actual
Toluene	0.470	0.483
40% Oleum	2.118	2.519
99% Nitric acid	0.547	0.787
60% Nitric acid	0.955	0.542

a. Adapted from Gilbert 1980.

TABLE 3.2. COMPOSITION OF NITROBODY IN SIX STAGES OF TNT MANUFACTURE BY THE RADFORD PROCESS[a]

Nitrobody	Composition (%) at Stage					
	1	2	3	4	5	6
	50–55[b,c]	70	80–85	90	95	100
Mononitrotoluene	77.1	–	–	–	–	–
Dinitrotoluene	18.2	70.9	30.4	10.3	1.6	0.2
Trinitrotoluene[d]	4.2	28.9	69.3	89.5	98.2	99.7

a. Adapted from Gilbert 1980.

b. Temperature in °C.

c. Latest information from Radford AAP indicates 25–60°C (Pal 1984).

d. Includes oxidation products.

3.1.1 White Compound

One of the problem areas in TNT manufacture is the formation of a so-called "white compound" (2,2'-dicarboxy-3,3',5,5'-tetranitro- azoxybenzene) primarily in nitrator vessel number three of the newly modified Radford process (vessel number two of the original Radford process with gravity separators). The mechanism of formation of trinitrobenzyl alcohol, trinitrobenzaldehyde, trinitrobenzoic acid, α-nitrato-toluene, and white compound is shown in Figure 3.4. According to Simons et al. (1977), the initial oxidation products of dinitrotoluene and trinitrotoluene, di- and trinitrobenzyl alcohol, and di- and trinitrobenzaldehyde appear to be the important precursors of white compound.

The precipitation of white compound on the nitrator cooling coils eventually necessitates a shutdown operation followed by a cleanup with sellite. However, 6 weeks of operation are possible before the line must be shut down for maintenance (Pal 1984).

It may be possible to minimize the formation of the white compound by controlling the experimental parameters. Simons et al. (1977) observed that NO_2 is linked to side chain oxidation and thus to white compound. Nitrogen flushing in anhydrous mixed acids does not lower the total oxidation but seems to suppress the formation of dinitrobenzalehyde, which may be a precursor of the white compound. This procedure could be useful in minimizing the formation of white compound in nitrator vessel number three. It is interesting to note that this nitrator vessel shows the highest NO_x emission, 29,500 ppm (see Table 5.1).

3.1.2 Impurities in TNT

Impurities present in TNT manufactured by continuous nitration and purification at Radford AAP are listed in Table 3.3 (Gilbert 1980). This table shows the approximate maximum nominal concentration of impurities in the crude and finished material. All five isomers of 2,4,6-TNT are present in the crude TNT, the major contributors being 2,4,5- and 2,3,4-TNT. The total amount of isomers of 2,4,6-TNT is reduced from 4.8 percent in the crude to less than 0.20 percent in the finished product after sellite purification (Bolleter 1985) (see Section 3.1.4). Six dinitrotoluenes and 1,3-dinitrobenzene, present as a result of incomplete nitration, are not removed appreciably by sellite treatment. 2,4,6-Trinitrobenzoic acid and the white compound (see Section 3.1.1) are removed, probably because of their solubility in sellite at alkaline pH. The last three compounds in Table 3.3 are not present in the crude TNT but are created during sellite treatment. Total impurities represent 7.53 percent of the crude TNT and 3.24 percent of the finished TNT (Gilbert 1980).

1,3,5-Trinitrobenzene, 2,4,6-trinitrobenzyl alcohol, 2,4,6-trinitrobenzalehyde, 2,4,6-trinitrobenzoic acid, and α-nitrato-2,4,6-trinitrotoluene are formed as a result of oxidation of the methyl group during nitration. Of these, only 2,4,6-trinitrobenzoic acid is removed appreciably by sellite treatment (Gilbert 1980).

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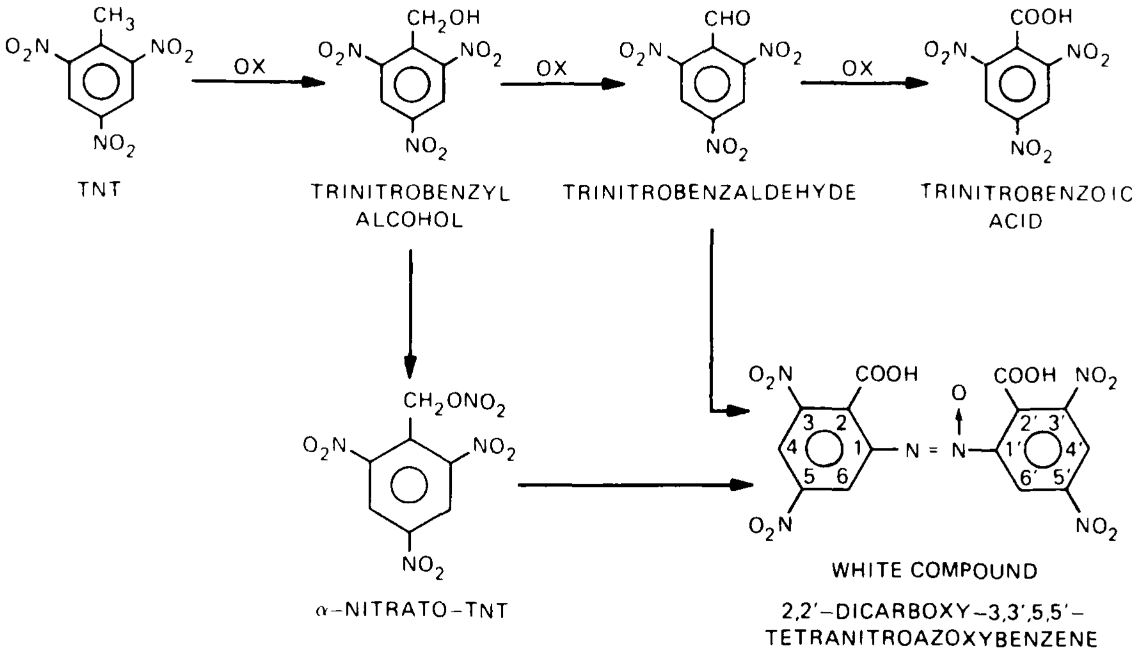

Figure 3.4. Mechanism for formation of white compound. Adapted from Bolleter 1971.

TABLE 3.3. IMPURITIES PRESENT IN TNT PREPARED BY CONTINUOUS NITRATION AND PURIFICATION[a,b]

Compound	Approximate Maximum Nominal Concentration (%)[c] Crude	Finished
2,4,5-Trinitrotoluene[d]	2.50	0.30
2,3,4-Trinitrotoluene[d]	1.75	0.20
2,3,6-Trinitrotoluene[d]	0.50	0.05
2,3,5-Trinitrotoluene[d,e]	0.05	0.05
2,6-Dinitrotoluene	0.25	0.25
2,4-Dinitrotoluene	0.50	0.50
2,3-Dinitrotoluene	0.05	0.05
2,5-Dinitrotoluene	0.10	0.10
3,4-Dinitrotoluene	0.10	0.10
3,5-Dinitrotoluene	0.01	0.01
1,3-Dinitrobenzene	0.02	0.02
1,3,5-Trinitrobenzene	0.15	0.10
2,4,6-Trinitrobenzyl alcohol	0.25	0.25
2,4,6-Trinitrobenzaldehyde	0.25	0.25
α-Nitrato-2,4,6-trinitrotoluene	0.10	0.10
Tetranitromethane	0.10	none
2,2'-Dicarboxy-3,3',5,5'-tetranitroazoxybenzene (white compound)	0.35	0.05
2,2',4,4',6,6'-Hexanitrobibenzyl	none	0.40
3-Methyl-2',4,4',6,6'-pentanitrodiphenylmethane	none	0.40
3,3',5,5'-Tetranitroazoxybenzene	none	0.01

a. Data from Radford AAP.

b. Adapted from Gilbert 1980.

c. Concentrations listed are the maximum possible. Actual values are much lower.

d. The presence of these impurities in finished TNT is possible, but they are usually not present (Bolleter 1985).

e. The 3,4,5-isomer has also been identified in crude TNT to the extent of 0.006 percent.

By the use of ^{14}C-labeled TNT, it was shown that 54.2 percent of the tetranitromethane comes from the aromatic C attached to the methyl group, 8.3 percent from each of the C atoms connected to nitro groups, 7.4 percent from each of the C atoms attached to H, and 6.1 percent from the methyl group (McDonnell 1978).

Di- and trinitrocresols have been reported to be among the impurities present in crude TNT (Urbanski 1983a). They are mainly formed during the nitration of toluene to mononitrotoluene. Trinitrocresol may be removed from TNT by mild alkali washing (e.g., with $NaHCO_3$ or a sodium sulfite solution). It is noteworthy that nitrocresols are not found in crude TNT as manufactured at Radford AAP (Table 3.3).

3.1.3 Isomers of TNT

Table 3.4 lists the six isomeric forms of TNT. The 2,4,6-TNT or α-TNT is the isomer of military interest. The other five isomers are formed during the manufacture of TNT. The most abundant is the 2,4,5-(γ) isomer followed by the 2,3,4-(β), 2,3,6-(η), 2,3,5-(ε), and 3,4,5-(δ) isomers (Gilbert 1980). The reaction of the reactive m-isomers with nucleophilic reagent sodium sulfite is illustrated in Figure 3.5.

α-TNT is not totally inert towards sulfite. It reacts to form, especially at a higher pH, the water soluble Jackson-Meisenheimer complex (Gilbert 1980).

TABLE 3.4. TNT ISOMERS[a]

Isomer	Position of Reactive Nitro Group
2,4,6- (α)	None
2,3,4- (β)	3
2,4,5- (γ)	5
3,4,5- (δ)	4
2,3,5 (ε)	2
2,3,6 (η)	3 (?[b])

a. Adapted from Gilbert 1980.

b. Best estimate of position.

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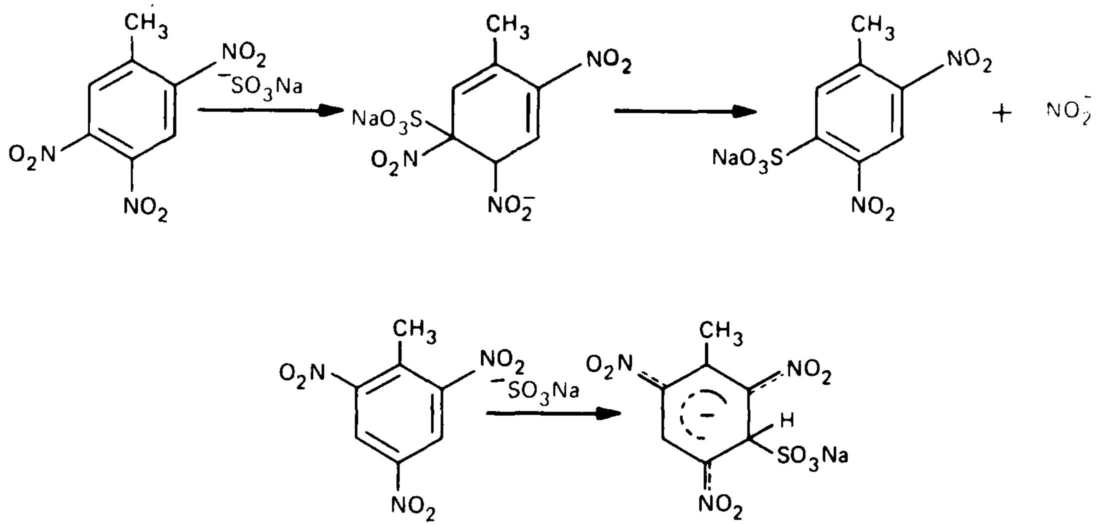

Figure 3.5. Reaction of TNT and its meta isomer with nucleophilic sodium sulfite. Adapted from Urbanski 1983a.

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3.1.4 Sellite Treatment

The impurities in TNT must be removed prior to military use to prevent exudation (Gilbert 1980). This is achieved by the treatment of crude TNT with aqueous sodium sulfite. Crude TNT is first washed with process water and then treated with sodium sulfite in two stages as indicated in Figure 3.1 and in more detail in Figure 3.6. It is very important to control the pH during sellite treatment. At pHs higher than 7.5, α-TNT forms a water soluble complex with sulfite, resulting in a yield loss of TNT (see Section 3.1.3) (Figure 3.7). At pHs higher than 7, more of the by-products 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) and 3-methyl-2'4,4',6,6'-pentanitrodiphenylmethane (MPDM) are formed (Figure 3.8). Figure 3.8 is a revision of the corresponding figure in Gilbert (1980) based on the data furnished by Dr. Bolleter at Radford AAP (as reported by Chandler et al. 1972). The reactions leading to the formation HNBB and MPDM are shown in Figure 3.9. The nitro groups in a portion of TNT are the oxidizing agent (Gilbert 1980).

The impurities HNBB and MPDM are insoluble in aqueous sellite and therefore remain in the finished TNT. At pH 9, over 0.5 percent of the two by-products are formed. This amount of impurity results in the lowering of the set point of TNT by about 0.2°C. This is equivalent to about 0.4 percent of dinitrotoluene (DNT) in the final product. Hence, if one can reduce the formation of these products, a much higher concentration of DNT will be tolerated to still give a product with a set point of 80.20°C or above as required in the specification (Bolleter 1971).

In the Radford process, TNT is contacted at a molten stage (>80°C) with sellite containing about 0.1 parts of anhydrous sodium sulfite per part of TNT (Gilbert 1980). This corresponds to about four times the theoretical amount required according to the reaction described in Section 3.1.3. The British ROF process also employs continuous purification using a compartmented reactor. However, TNT is contacted as a solid at 67.5°C, rather than as a liquid at >80°C as in the Radford process. This is said to result in a higher yield of purer TNT with a requirement of about two-thirds as much sellite. HNBB and MPDM are not formed under these conditions. In the ROF process, advantage is taken of the fact that the asymmetric isomers form a eutectic which diffuses to the crystal surface. The possibility of adoption of this procedure was discussed with Dr. Chandler and Mr. Morris at the Radford AAP. Dr. Chandler expressed the opinion that the ROF process is unsuitable for large-scale production as practiced in the United States. In a large-scale continuous process it is much easier to handle TNT in a molten stage rather than a solid stage. On the other hand, Urbanski (1983a) has commented that the handling of liquid TNT requires more safety measures than does the handling of solid TNT, although the fact that detonation in molten TNT proceeds only with great difficulty reduces the danger (Urbanski 1983a).

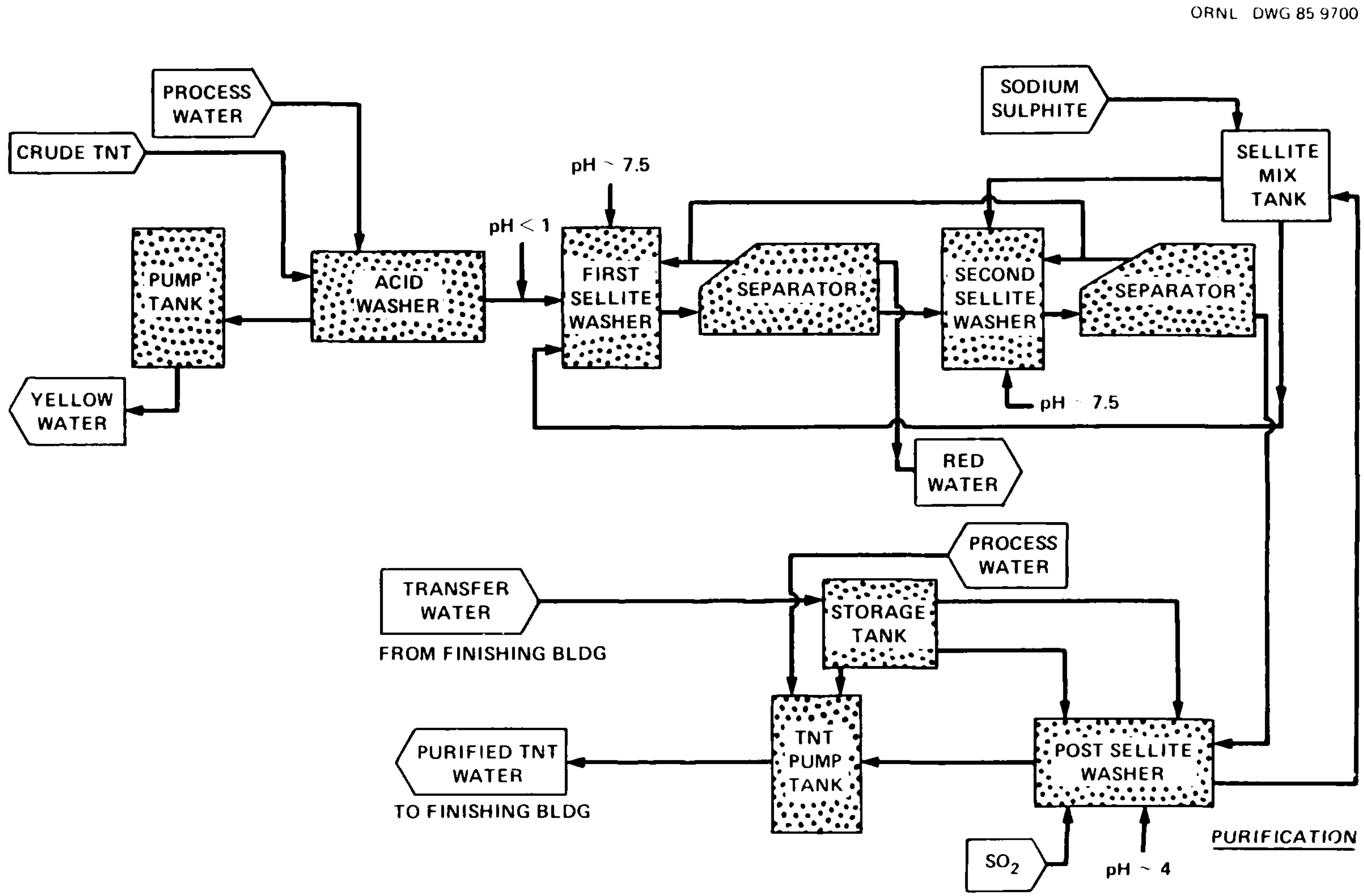

Figure 3.6. TNT purification flow scheme. Adapted from Gilbert 1980.

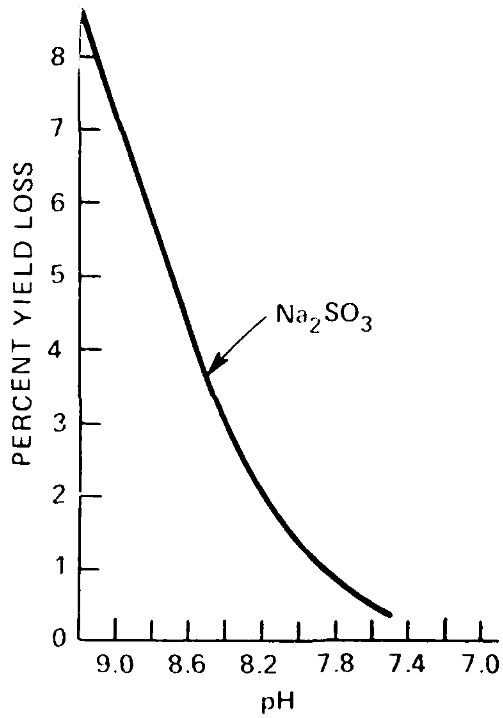

Figure 3.7. Effect of pH on yield loss of TNT during sellite treatment. Adapted from Gilbert 1980.

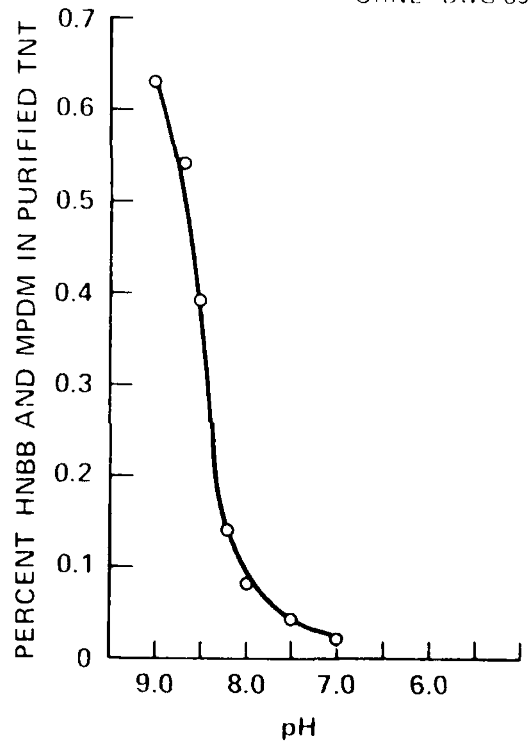

Figure 3.8. Effect of pH on byproduct formation during sellite treatment of TNT. HNBB = 2,2',4,4',6,6'-hexanitrobibenzyl and MPDM = 3-methyl-2'4,4',6,6'-pentanitrodiphenylmethane. Adapted from Gilbert 1980.

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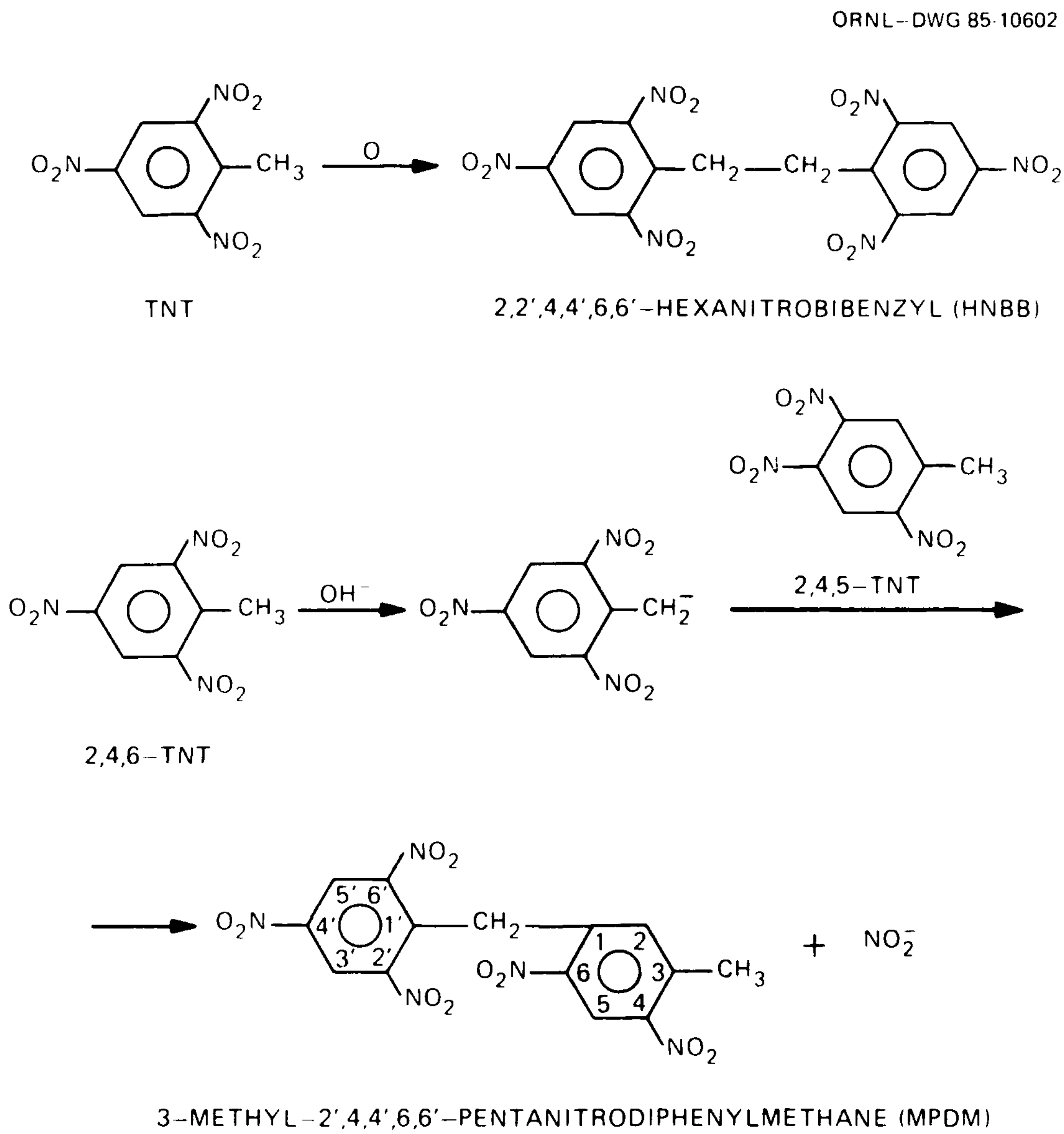

Figure 3.9. Reactions leading to formation of HNBB and MPDM. Adapted from Bolleter 1971.

3.1.5 Exudation of TNT

Purification of TNT is necessary to improve its stability and to remove impurities (e.g., TNT isomers and lower nitrated substances) which can easily form oily exudation products (TNT-oil). The exudation product is very undesirable for the following reasons (Urbanski 1983a):

1. Exudation produces porosity of the TNT charge and reduces its density and hence its explosive effect. In artillery shells it can produce a dislocation of the charge on firing, compression of the air included in the cavities, and premature explosion. However, Bolleter has disputed this;

2. The exudate can penetrate the threaded part of the shell and form "fire channels" through which the ignition of propellant can ignite the charge; and

3. The exudate can possibly reduce the detonating power of the gaine.

One current method (Gilbert 1980) of testing for exudation consists of tightly wrapping a 1 inch x 5 inch casting of the explosive sample with Whatman No. 1 filter paper and sealing it hermetically in a heavy-walled aluminum cylinder. The sample is then held at 71°C for six days. The exudate absorbed by the paper is measured. Military grade TNT typically shows 0.6 to 1.2 percent exudate, although Gilbert (1980) states that this upper limit may be higher.

A typical analysis of the exudate from specification-grade TNT, made at Radford AAP by the continuous process, is as follows (Gilbert 1980):

2,4,6-TNT (α)	88.1%
2,3,4-TNT (β)	1.99%
2,4,5-TNT (γ)	0.67%
2,4-DNT	7.65%
2,6-DNT	0.98%
2,5-DNT	0.19%
HNBB and MPDM	0.1-0.5%

Exudation is minimized by purifying TNT by careful "selliting" in the Radford process (see Section 3.1.4). Another way to minimize exudation is to add small amounts (0.6 percent) of cellulose esters or polyurethane to preclude exudate by absorption (Gilbert 1980).

3.1.6 Recycling of off-specification TNT

Approximately 35,000 lb per month of off-specification TNT is generated per continuous production line at Radford. Currently, this material is incinerated. Incineration costs as well as product loss could be significantly reduced or eliminated if an effective means of recycling and upgrading existed. Although the TNT-production-operating personnel feel that recycling and upgrading are feasible, such a technology has yet to be developed (Renard 1984), but was being researched in FY 1985 (Renard 1985) (see page A-20). According to Bolleter (1985), most off-specification TNT is cycled back into the process. Gilbert et al. (1982) may be of interest in this connection.

3.2 MANUFACTURE OF RDX AND HMX

In the United States, RDX is mainly manufactured at the Holston AAP. The continuous Bachmann process, which is very similar in principle to the "KA-method" developed by Koffler in Germany, is the method of manufacture. The overall reaction is presented below (Urbanski 1983e; Lindner 1980):

$$C_6H_{12}N_4 + 2\ NH_4NO_3 + 4\ HNO_3 + 6\ (CH_3CO)_2O \xrightarrow{\sim 70°C} 2\ (CH_2NNO_2)_3 + 12\ CH_3COOH$$

hexamine, ammonium nitrate, nitric acid, acetic anyhydride, RDX, acetic acid

An overview of the process of RDX manufacture is shown in Figure 3.10. HMX is also produced from the same reactants by varying the ratio of ammonium nitrate to hexamine and lowering the reaction temperature to 44°C (Lindner 1980).

3.2.1 Manufacture - D Buildings

In the manufacture of RDX and HMX at Holston AAP, the following raw materials are fed to a stainless steel reactor: (1) hexamine/acetic acid, (2) nitric acid/ammonium nitrate, (3) acetic acid, and (4) acetic anhydride. The ensuing reaction is exothermic, and the heat evolved is removed by the reactor jacket cooling water and by the internal cooling coil. The slurry from the reactor enters a temperature-controlled aging tank where further reactions occur. Slurry from the aging tank drains into four simmer tanks in series (HMX production involves two simmer tanks in parallel) where dilution liquid is added to maintain an acetic acid concentration of 63 ± 3 percent. The content is simmered at 108°C and then cooled to 50°C. The last simmer tank serves as a holding tank from which the slurry is pumped to the E Buildings, where it is washed, filtered, and reslurried for transfer. Flow diagrams of RDX and HMX manufacture are shown in Figures 3.11 and 3.12, respectively (Carpenter et al. 1978b).

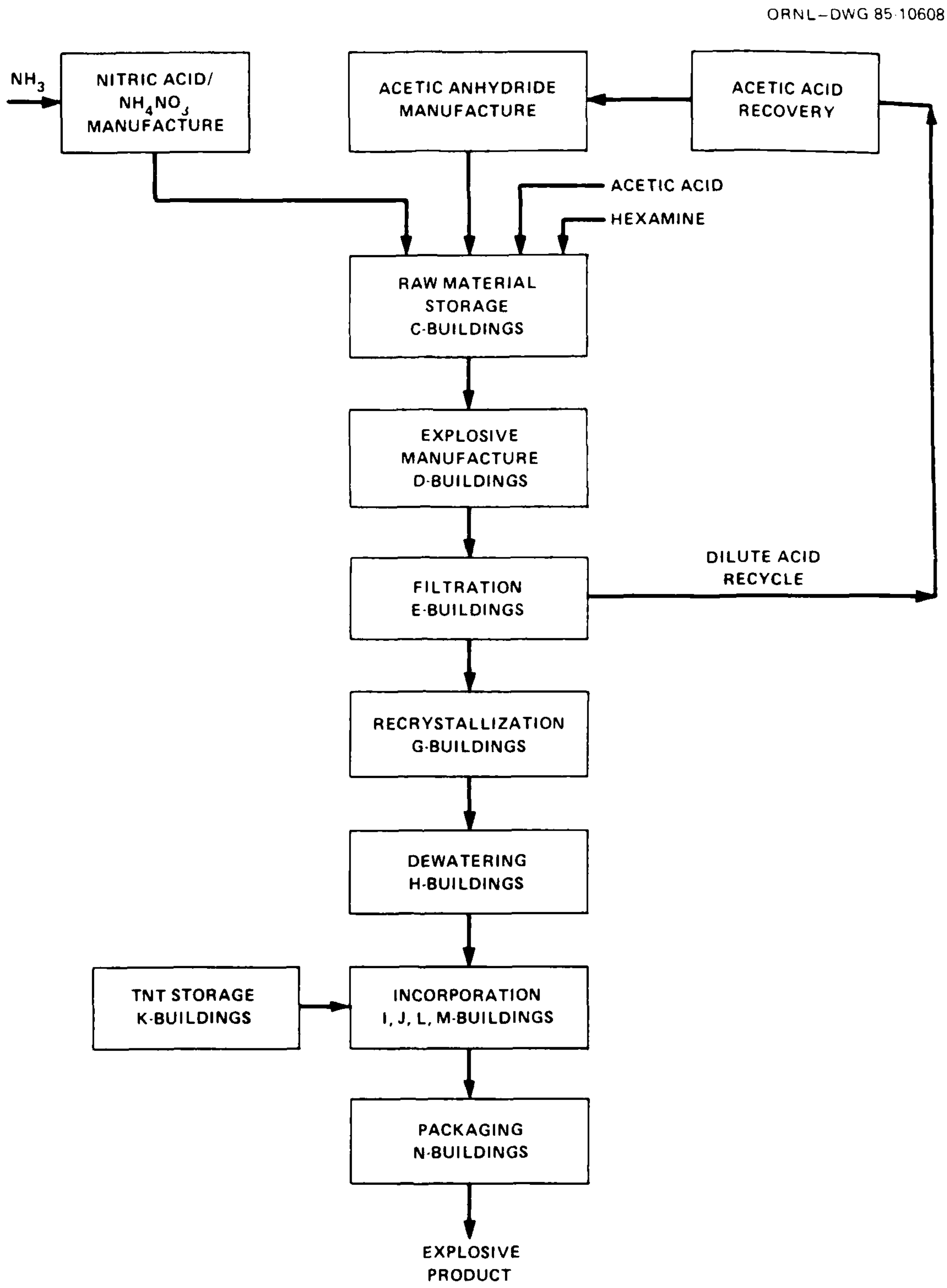

Figure 3.10. Overview of RDX manufacturing operations at Holston AAP. Adapted from Carpenter et al. 1978b.

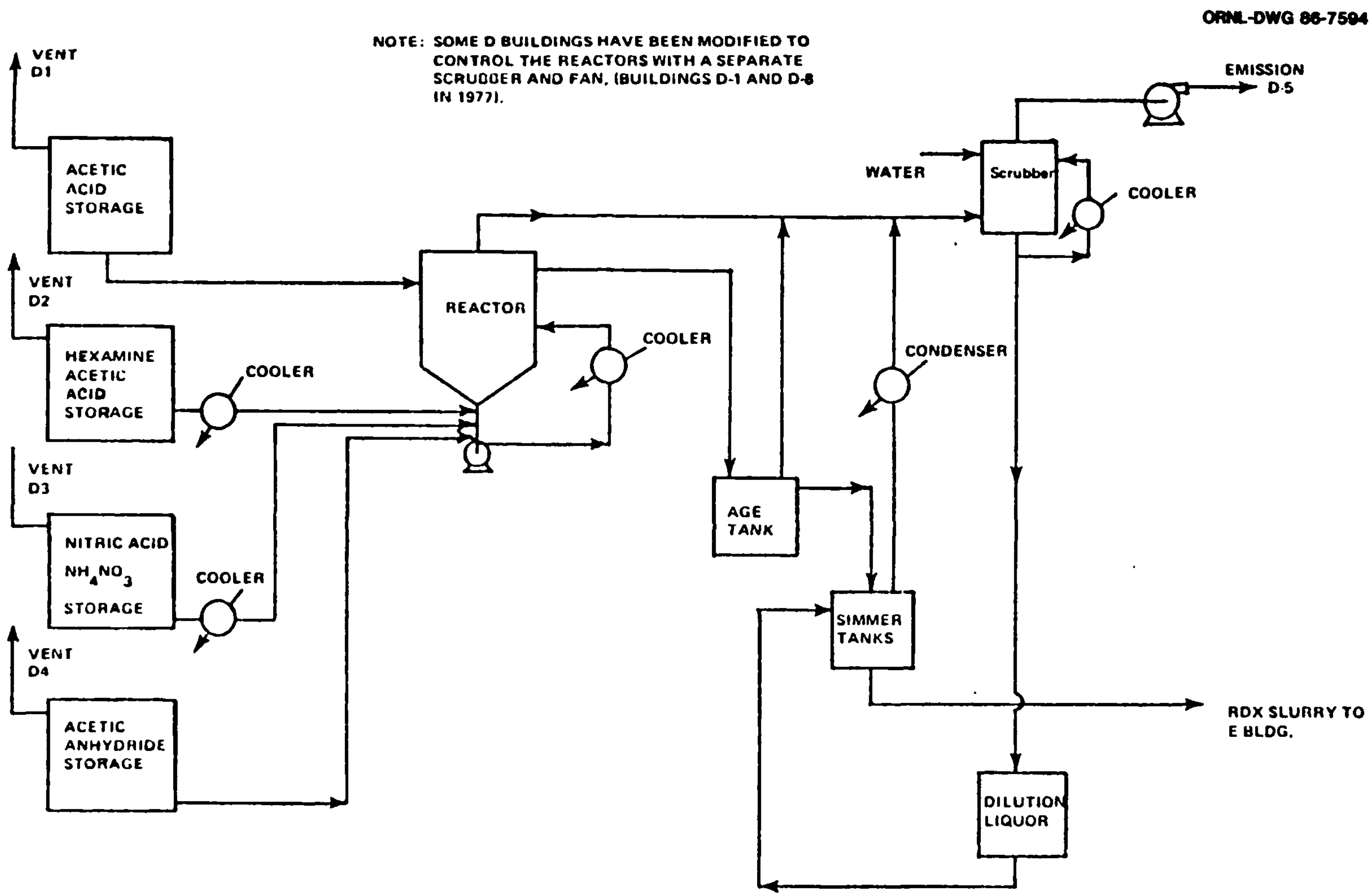

Figure 3.11. RDX manufacture - D buildings. Adapted from Carpenter et al. 1978b.

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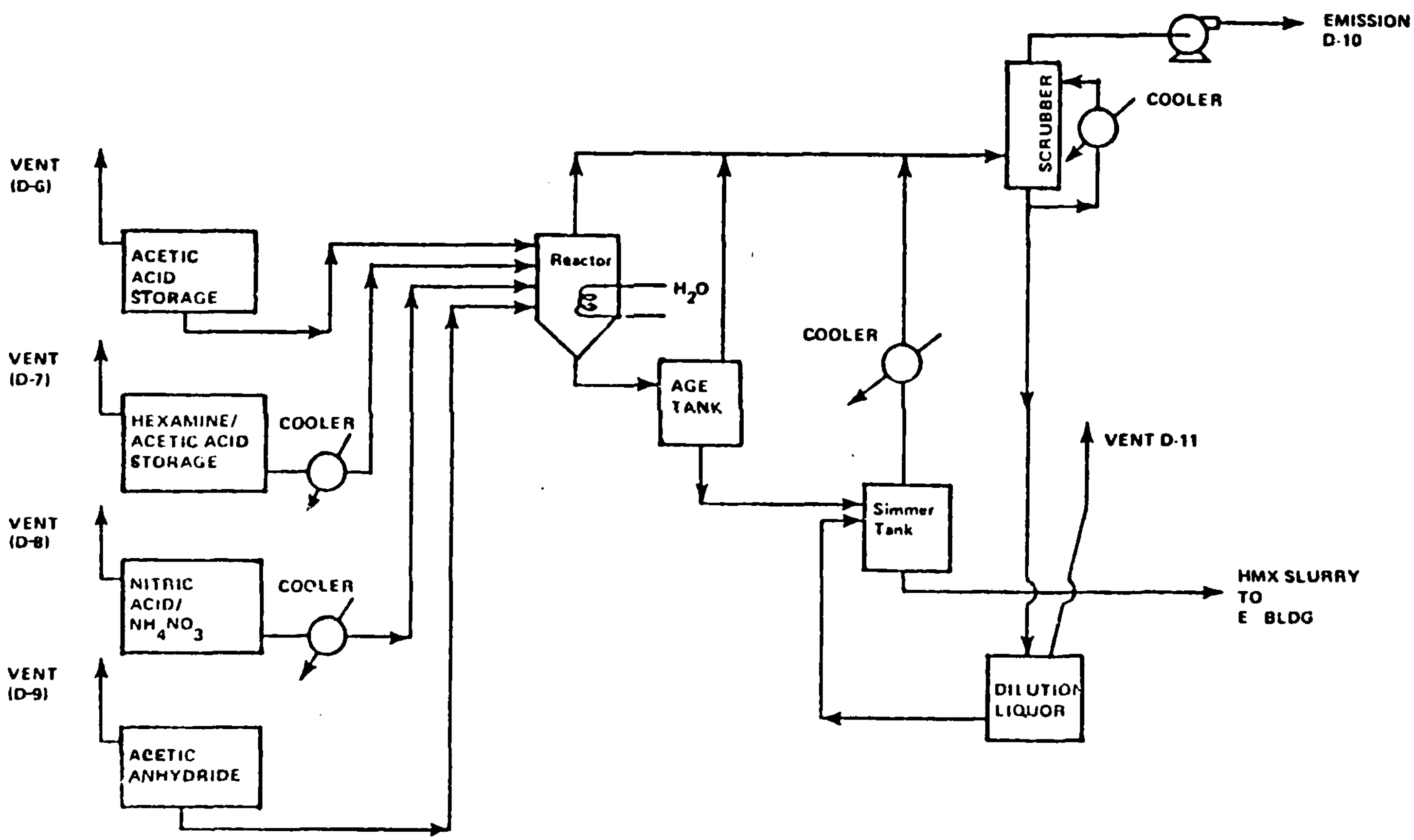

Figure 3.12. HMX manufacture - D buildings. Adapted from Carpenter et al. 1978b.

3.2.2 Explosive Wash - E Buildings

In the E Buildings, the RDX slurry is allowed to settle and to be filtered; the filtrate is 60 percent acetic acid (the filtrate recovered from HMX manufacture is 80 percent acetic acid). The latter is diluted to 60 percent acetic acid so that B Buildings (denoted as acetic acid recovery in Figure 3.10) will receive a relatively uniform feed from all E Buildings. In the second step, the explosive cake is slurried with water and filtered. This filtrate is sent to the D Buildings as dilution liquor. In the third step, the explosive cake is reslurried with fresh water and pumped into the G Buildings. A flow diagram is shown in Figure 3.13 (Carpenter et al. 1978b).

3.2.3 Explosive Recrystallization - G Buildings

Crude RDX/HMX from an E Building is dissolved and recrystallized from a suitable solvent to yield the desired crystalline size and form. Recrystallization also reduces the occluded acid to less than 0.02 percent. The flow plan of the processing area is shown in Figure 3.14. The explosive is fed into a dissolver containing a specified amount of cyclohexanone, acetone, or toluene, depending on the type of crystallization desired. The dissolver contents are simmered and then transferred to a preheated still. The solvent is distilled off, condensed, and recycled. Vapors from the primary condenser together with the vapors from the dissolver are condensed in a secondary condenser and returned to the dissolver. Uncondensed vapors are vented to the atmosphere through a flame arrestor. The batch is then cooled to crystallize RDX (Carpenter et al. 1978b).

3.2.4 Acetic Acid and Acetic Anhydride

The dilute (60 percent) acetic acid recovered from the manufacture of RDX/HMX is concentrated by azeotropic distillation with n-propyl acetate. The concentrated acid (>99 percent) is vaporized and fed to cracking furnaces. Eighty percent of the entering acetic acid vapor is cracked to ketene and water, and about 2 percent is cracked into various light hydrocarbons. The unreacted acetic acid and water are condensed out of the vapor stream and recycled for recovery of acetic acid. The vapor stream enters a scrubbing train where the ketene reacts with acetic acid forming crude acetic anhydride. It is purified by distillation in a two-stage refining column (Carpenter et al. 1978b).

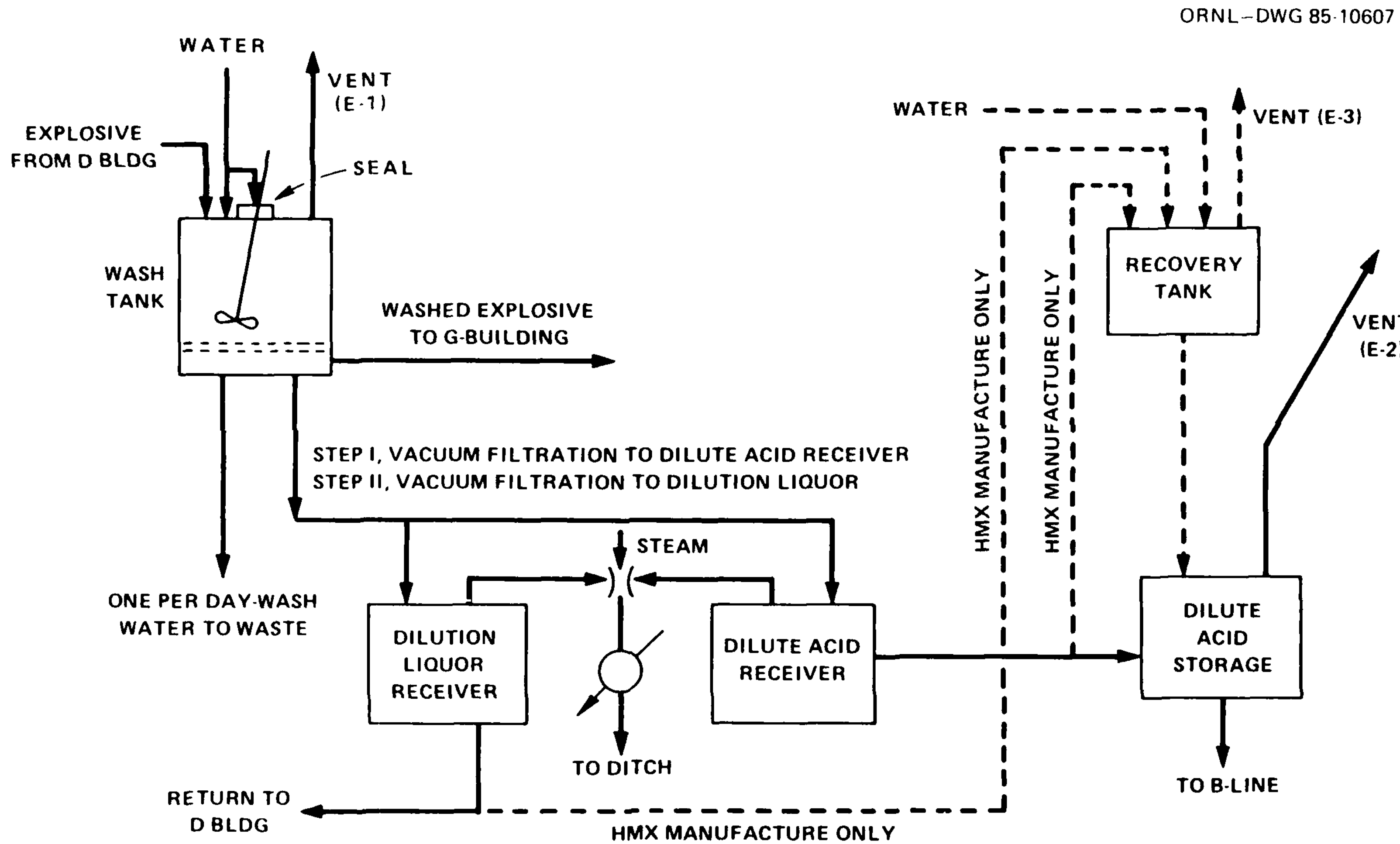

Figure 3.13. RDX/HMX explosive wash – E buildings. Adapted from Carpenter et al. 1978b.

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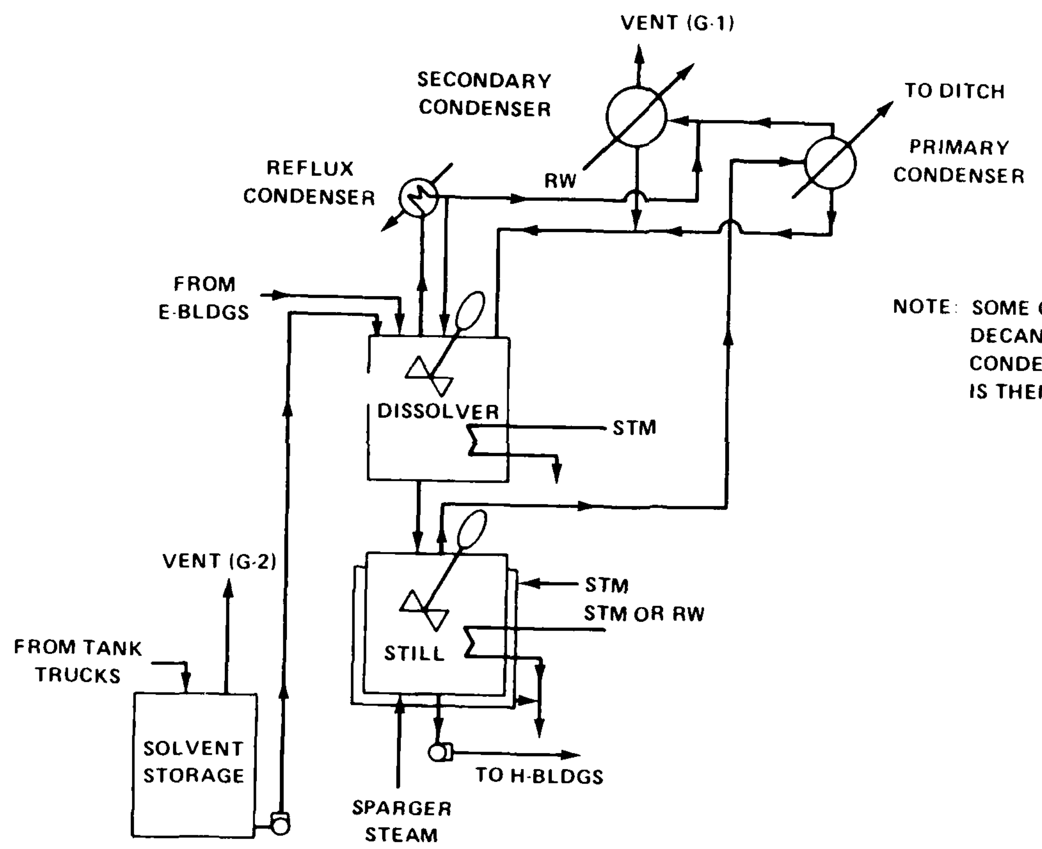

NOTE: SOME G BUILDINGS UTILIZE AN EXTERNAL DECANTER VESSEL TO RECEIVE THE PRIMARY CONDENSER CONDENSATE. THE CONDENSATE IS THEN PUMPED BACK TO THE DISSOLVER.

Figure 3.14. RDX/HMX recrystallization - G buildings. Adapted from Carpenter et al. 1978b.

3.2.5 Nitric Acid and Ammonium Nitrate Manufacture

Dilute nitric acid (about 60 percent) obtained from the ammonia oxidation plant (see Section 5.1.1) is concentrated for reuse in explosive manufacture by an extractive distillation process based on magnesium nitrate. Weak nitric acid and concentrated (72 percent) magnesium nitrate solution are fed to the top of a three-stage stripping column together with the intermediate (80 to 90 percent) nitric acid from the base of a rectifying column. Overhead vapors from the stripping column are condensed and split into reflux and product streams. The product portion (99 percent nitric acid) is cooled further in cascade coolers. The uncondensed overhead vapors from the strong nitric acid condensers are led to a rectifying column and scrubbed with water before being vented to the atmosphere. The bottoms from the stripping column contain approximately 60 percent magnesium nitrate and less than 0.1 percent nitric acid. This solution is first concentrated to 64 percent strength by heating in a steam-heated boiler. Further concentration to the original feed strength of 72 percent is carried out in a vacuum evaporator (Carpenter et al. 1978b).

Ammonium nitrate is produced at the Holston AAP by the direct reaction of anhydrous ammonia with nitric acid in a circulating stream of ammonium nitrate solution. Heat of reaction is removed in a series of five water cooled heat exchangers (Carpenter et al. 1978b).

3.3 SULFURIC ACID REGENERATION

Spent or weak sulfuric acid along with liquid sulfur is used as a feed stock to produce oleum and concentrated sulfuric acid. In this process, the weak sulfuric acid, liquid sulfur, and fuel oil are mixed with preheated air and burned to provide a combustion product with 8.5 percent SO_2. The heat of combustion is partially recovered in steam generation. The gas mixture is first humidified and cooled in a tower using 35 percent sulfuric acid. It is then dried by chilling followed by treatment with 93 percent sulfuric acid in a tower. The purification, cooling, and moisture control occur on the intake side of the acid plant blower. The converter and absorption towers are on the discharge side of the blower. The converter contains the catalyst V_2O_5 which promotes the conversion of SO_2 to SO_3. This part of the regeneration process can be carried out in two ways: (1) single contact/single adsorption (SE/SA) system or (2) double contact/double absorption (DC/DA) system as adopted in the Radford plant. The latter is presented schematically in Figure 3.15 (Carpenter et al. 1978c).

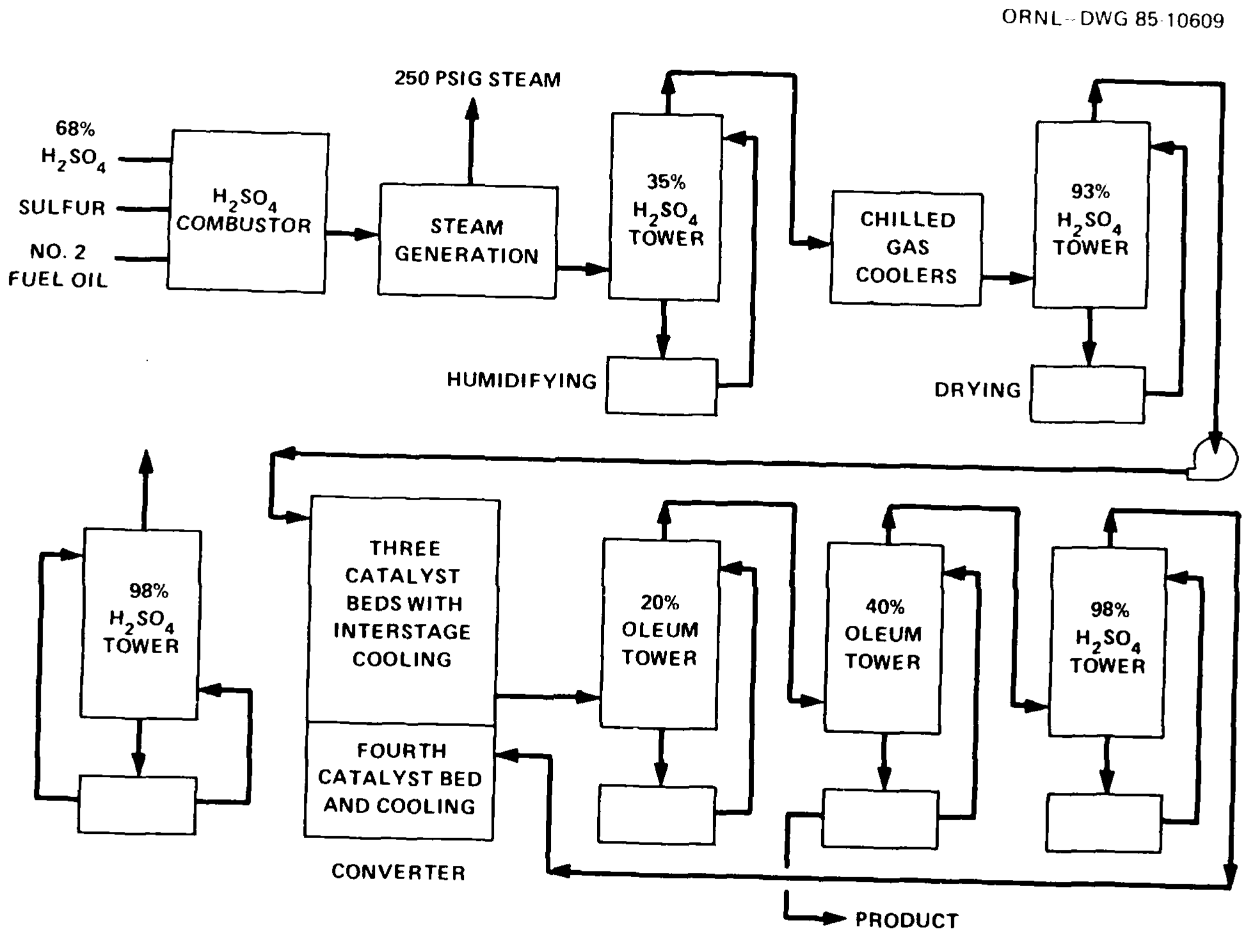

Figure 3.15. Radford AAP double contact/double absorption sulfuric acid regeneration plant. Adapted from Carpenter et al. 1978b.

4. SCENARIO OF THE ARMY POLLUTION ABATEMENT PROGRAM

The AAPs built to meet the emergency of World War II relegated environmental degradation to a minor concern. Increased public awareness of environmental pollution during the late 1960s resulted in Executive Order 11597, dated February, 1970 and later superseding orders which required all federal facilities to conform to federal environmental standards (Ziegler 1980). This led the Army to embark on a plan to modernize the production base and reduce or eliminate objectionable pollutants from munitions waste discharges. The magnitude of this modernization effort has been addressed by Novak (1983). The Army has 35 installations located in 22 different states and collectively these facilities compose one of the largest industrial manufacturing complexes in the United States. Pollutants produced at these installations range from propellant and chemical contaminants to heavy metals and petroleum residues.

There appears to be two complementary Army pollution abatement programs (USATHAMA 1984) - the Manufacturing Methods and Technology Pollution Abatement Technology Program (MMTPAT) (Figure 4.1) and the Pollution Abatement and Environmental Control Technology Program (PAECT) (Figure 4.2). All the agencies identified in these two figures interact with each other in the manner shown. In the MMTPAT program, a GOCO or GOGO plant occupies the central position (Figure 4.1) whereas, in the PAECT program, all the interactions are built around the USATHAMA Environmental R&D Team (Figure 4.2). The function of these two programs has been defined in USATHAMA (1984) as follows:

> The Pollution Abatement and Environmental Control Technology Programs conduct research studies to develop and recommend technology to enable Army industrial facilities to achieve and maintain environmental compliance during their operation. The Manufacturing Methods and Technology programs seek to implement suitable technology for the same purpose by conducting more advanced development than that normally performed in the PAECT program. Each program has its separate function in achieving a common goal. Close coordination and integration of efforts is required for effective development of usable improved technology in the most cost-effective manner.

A summary of the current MMTPAT program is shown in Table 4.1 (Renard 1984). Total funding for these 17 projects during the period FY 1981 through FY 1985 amounts to $10,482,000. The PAECT program summary for the period FY 1984 through 1986, is quite lengthy and is thus presented as Appendix A (Renard 1984). Information is given on each project under the following headings: I. Task Description; II. Deficiency/Need That Task Addresses; III. Technology Development Plan; and IV. Plans for Technology Transfer/Implementation. A total of twenty different projects have been listed.

TABLE 4.1. SUMMARY OF MMT POLLUTION ABATEMENT PROGRAM[a]

Project No	Title	1981	1982	1983	1984	1985
1354	Sludge volume reduction and disposal	110[b]				
1711	Red phosphorous pollution abatement		125			
4061	Nitroguanidine process optimization			640		
4225	Red water pollution abatement	158				
4226	On-line monitors for water pollutants	433				
4231	In-plant reuse of pollution abated waters	461	313			
4364	Bio-sensors	258	290			
4298	Destruction of DNN from HSAAP B-line	470	390	295		
4489[c]	Advanced pollution abatement technology (Tasks 1, 2, 3, 5)		1,359	86	917	343
4309	Ammo F/Abrahms tank (white water abatement)		200			
4579	White water pollution abatement				500	
4556	On-line monitors				435	
4318	Environmental improvement-OSHA-nitrate esters					100
4564	Environmental control technology for AAPs					1,120
4616	PAC/activated sludge process					315
4612	Nitramine (LOVA) wastewater abatement					250
4511	Disposal of final sludge from acid recovery		304	582	478	
	TOTALS	1,890	2,981	1,063	2,330	2,218

a. Adapted from Renard 1984.

b. Values given in thousands of dollars.

c. The project No. 4489 consists of: Task 1 - disposal of wastewater treatment sludges; Task 2 - advanced pink water treatment; Task 3 - tertiary treatment of Holston wastewater, and Task 5 - advanced air emissions abatement. The Project No. 4564 consists of: Task 2 - solid waste (sludge) disposal technology; Task 3 - hydrogen peroxide treatment of AOP exhaust; Task 4 - assessment of technological advances for military unique pollutants, and Task 8 - pilot plant evaluation for treating detonator wastewaters at Kansas AAP.

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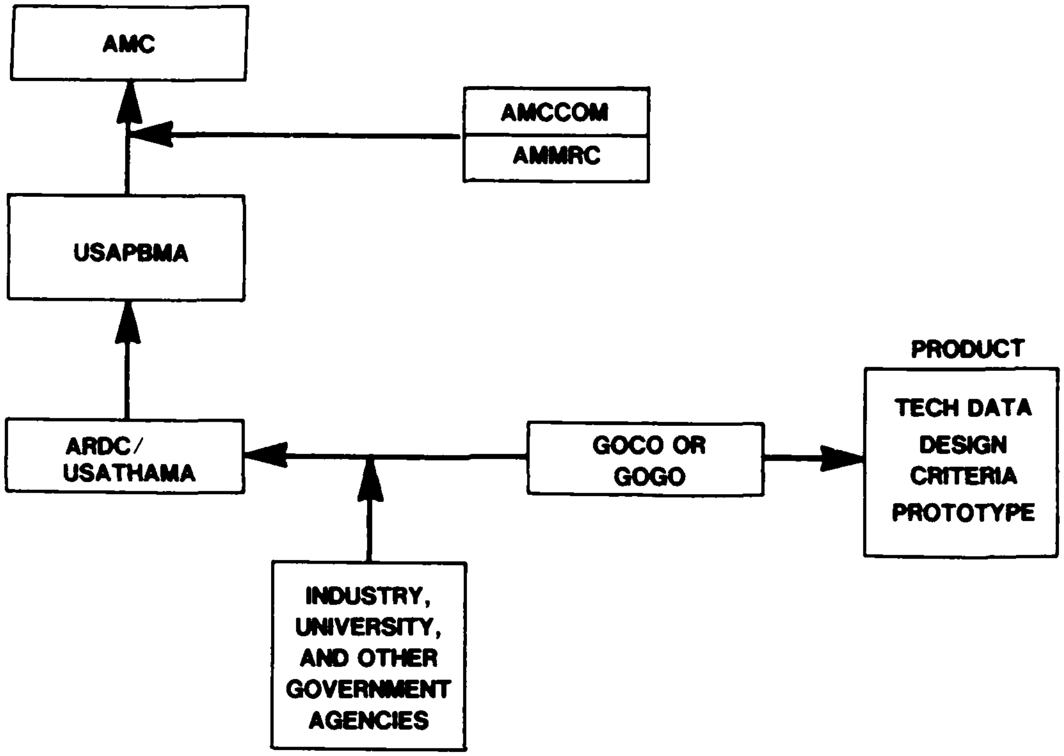

MMT - MANUFACTURING METHODS AND TECHNOLOGY
AMC - U.S. ARMY MATERIEL COMMAND
USAPBMA - U.S. ARMY PRODUCTION BASE MODERNIZATION AGENCY
AMCCOM - ARMY ARMAMENT MUNITIONS AND CHEMICAL COMMAND
AMMRC - ARMY MATERIALS AND MECHANICS RESEARCH
ARDC - ARMY ARMAMENT RESEARCH AND DEVELOPMENT CENTER
USATHAMA - U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY

Figure 4.1. Pollution abatement technology program. Adapted from USATHAMA 1984.

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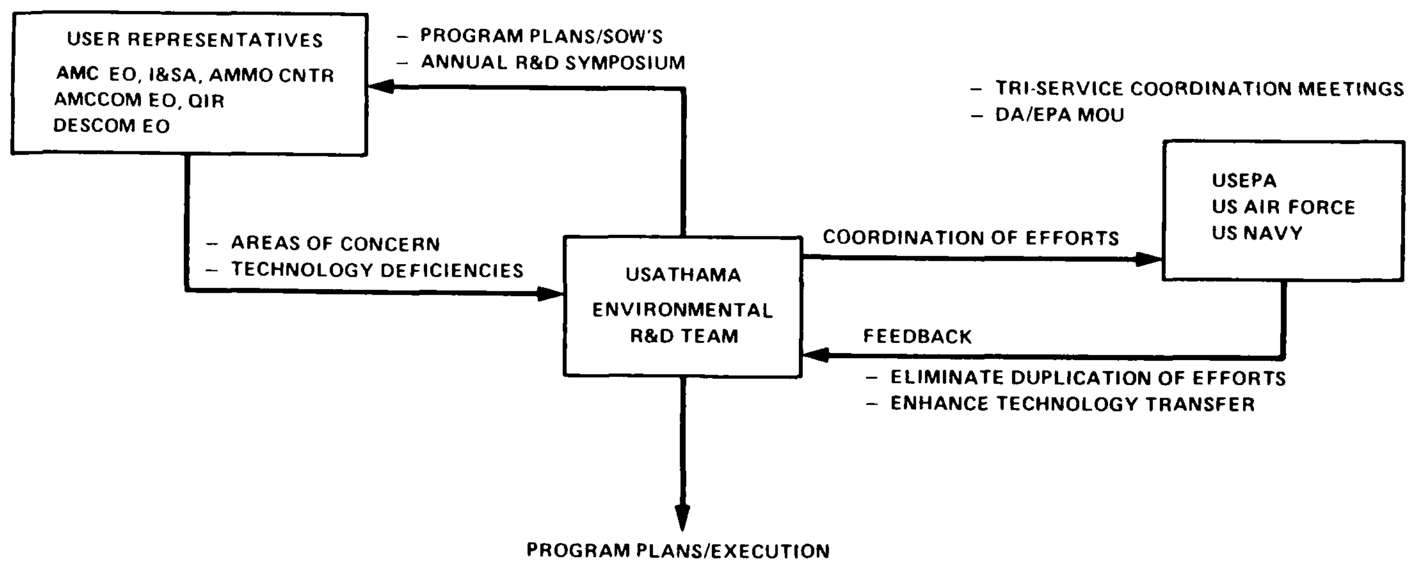

AMC – U.S. ARMY MATERIEL COMMAND
AMCCOM – ARMY ARMAMENT MUNITIONS AND CHEMICAL COMMAND
DESCOM – DEPOT SYSTEMS COMMAND
USATHAMA – U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
EO – ENVIRONMENTAL OFFICE
I&SA – INSTALLATION AND SERVICE ACTIVITY
USEPA – UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
DA/EPA MOU – DEPARTMENT OF ARMY/ENVIRONMENTAL PROTECTION AGENCY MEMORANDUM OF UNDERSTANDING

Figure 4.2. Pollution abatement and environmental control technology program interactions. Adapted from USATHAMA 1984.

5. AIR POLLUTANTS FROM ARMY AMMUNITION PLANTS

Major air pollutants encountered during the manufacture and processing of explosives and propellants include NO_x, SO_x, and organic vapors such as tetranitromethane, nitroglycerin, dimethylamine, methylamine, ethanol, acetone, and diethyl ether. Another source of air pollution is the incineration of wastes containing explosives and propellants (Hercules 1984b; Zeigler 1980; Carpenter et al. 1978a-d). An in-depth survey of specific air pollutants from TNT and RDX manufacture and incineration of waste explosives has been carried out by Carpenter et al. (1978a-d).

5.1 NITROGEN OXIDES

Air pollution in the form of NO_x occurs in the production of nitric acid from the ammonia oxidation plants (AOPS) and as by-products originating from nitric acid used in TNT and nitrocellulose manufacture (Zeigler 1980).

A discussion of the role of NO_x as an environmental pollutant (the reader may refer to an excellent review on the subject, DOE 1983) is beyond the scope of this document, but it is important to note the differences between nitric acid and sulfuric acid. Nitric acid originating from atmospheric reactions of NO_x is an important forest nutrient, whereas sulfuric acid is much less so. Assimilation of nitrate in the soil neutralizes the acidity so that nitric acid causes no long-term acidification. Experimental work at ambient levels has shown beneficial, than harmful, effects on plant growth (Innes 1984); however, Abelson (1984) has pointed out that NO_x is involved in photochemical reactions that lead to oxidants such as ozone that are highly toxic to plants and trees. Another consequence of acid rain caused by SO_2 and NO_x emission is that the acidity tends to raise aluminum ion levels more than calcium ion levels (from their insoluble salts). Excessive levels of aluminum have been found to be rather toxic (Williams 1984).

5.1.1 NO_x Emission from Ammonia Oxidation Plants

Ammonia oxidation plants produce dilute nitric acid, which is later concentrated to form >99 percent nitric acid. In the duPont units (total capacity, 500 ton/day of 100 percent acid at Holston AAP) air is compressed, heated, mixed with superheated ammonia, and passed over a specially developed platinum catalyst. Nitrogen oxide (NO) and water vapor are formed by the reaction. As this mixture is cooled in the condensers and absorption columns, oxidation of NO to NO_2 occurs. As the water vapor condenses it absorbs some NO_2 to form nitric acid (HNO_3), which is air-lifted through the column by compressed air. Water (steam condensate) is introduced at the top of the column to absorb most of the NO_2 (Carpenter 1978b).

A magnesium nitrate process is used to concentrate nitric acid at Holston AAP. Magnesium nitrate has an affinity for water, and the principle of a ternary system (magnesium nitrate, nitric acid, and water) is used to remove water from the acid by extractive distillation. Weak (61 percent) nitric acid

and a concentrated solution (72 percent) of magnesium nitrate are fed to the top of the three-stage stripping column together with the intermediate (80 to 90 percent) nitric acid from the base of the rectifying column. Overhead vapors from the stripping column are condensed and then divided into reflux and product streams. The product portion (99 percent nitric acid) is cooled further in cascade coolers. The uncondensed overhead vapors from the strong nitric acid condensers are led to a rectifying column and scrubbed with water before being vented to the atmosphere. The bottoms from the stripping column contain approximately 60 percent magnesium nitrate and less than 0.1 percent nitric acid. It is concentrated in two stages, first in a steam-heated reboiler and then in a vacuum evaporator, to 72 percent and recycled (Carpenter et al. 1978b).

Most of the NO_x originates from the exhaust gas from the ammonia oxidation process absorber and has been estimated to be 1720 lb/day per 500 ton of 100 percent nitric acid, assuming full mobilization (Carpenter et al. 1978b). This is equivalent to 3.44 lb/ton, well below the Virginia and the Tennessee regulatory limit (applicable to new plants) of 5.5 lb/ton of 100 percent acid (VAPCR 1983) but slightly exceeding the USEPA Performance Standard of 3.0 lb/ton of 100 percent acid (see Section 11.2).

5.1.2 NOx and Tetranitromethane Emission from TNT Plants

The NO_x emission from TNT plants is handled differently in the individual AAPs. Because the Radford AAP has the most modern TNT plant in the United States, treatment of NO_x in this plant is described below.

According to Carpenter et al. (1978c), the Radford AAP uses a five tower scrubbing system for each TNT line. The system is designed to recover NO_x and nitrobodies through the use of three different types of scrubbing towers-a water-fed bubble cap absorption tower, a sulfuric acid tower, and sellite towers. As shown schematically in Figure 5.1, fumes from the nitration and purification building are collected and introduced to the bottom of a water-fed bubble cap absorption tower. As the gases rise against the countercurrent flow of water, the NO_x will be absorbed to make 55 to 60 percent nitric acid. This weak nitric acid stream is returned directly to the production line. Two consecutive sulfuric acid towers are used to further scrub NO_x from the gas stream. The first tower uses 75 percent sulfuric acid, and the second tower uses 87 percent sulfuric acid. This contaminated sulfuric acid is blended into the spent acid recovery feed to recover the nitric acid. The exhaust gas is essentially free from NO_x at this stage but still contains tetranitromethane, which is removed by the two sellite towers. The reactions taking place in these three different types of towers are:

$$NO + NO_2 + O_2 + H_2O \text{ ----> } 2\ HNO_3 \qquad \text{(Farber 1976)}$$

$$NO + NO_2 + 2\ H_2SO_4 \text{ ----> } 2\ HNO{\cdot}SO_4 + H_2O \qquad \text{(Farber 1976)}$$

$$C(NO_2)_4 + Na_2SO_3 \text{ ----> } (O_2N)_3CSO_3Na + NaNO_2 \qquad \text{(Urbanski 1983e)}$$

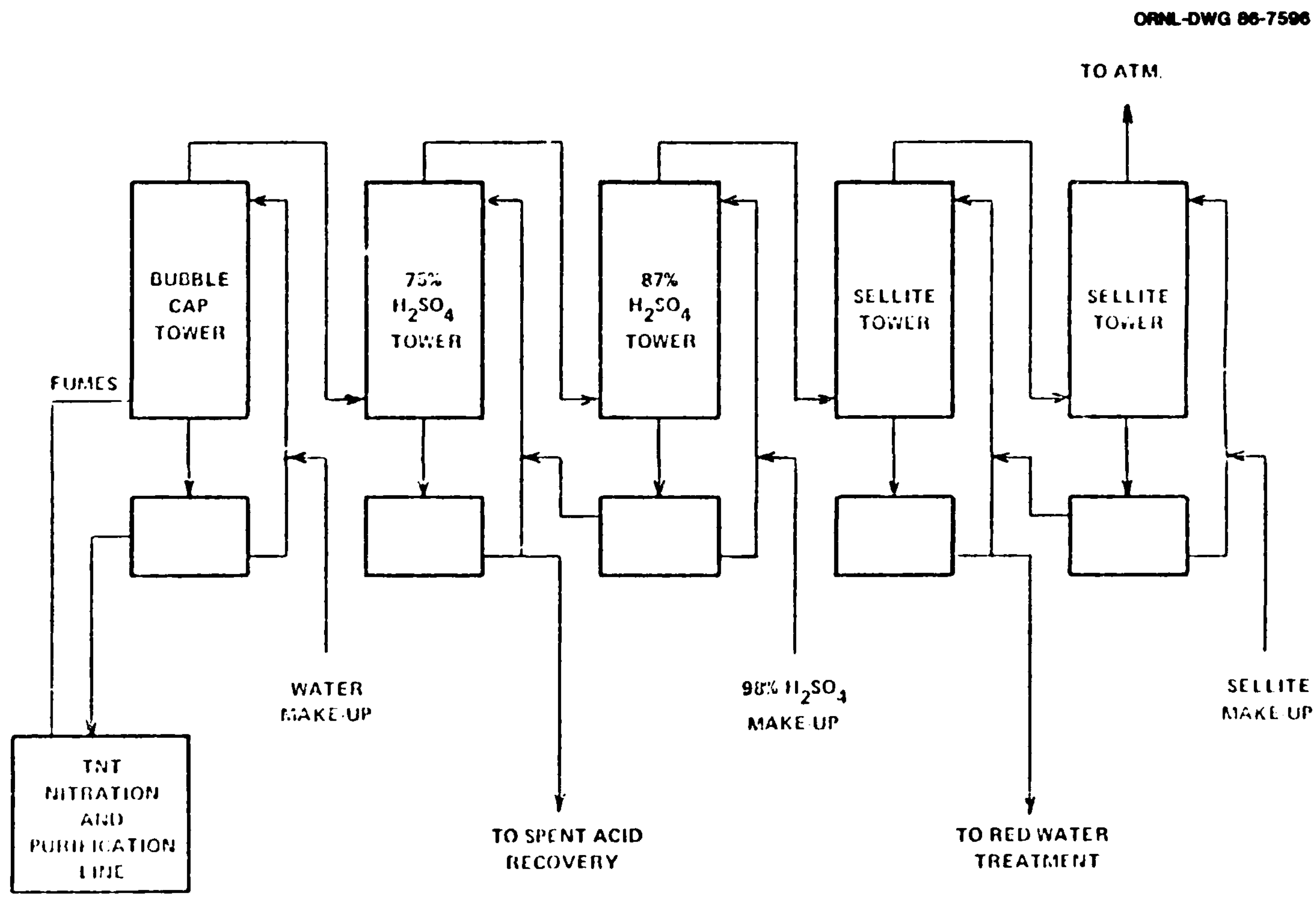

Figure 5.1. Radford AAP nitration and purification facilities. Adapted from Carpenter et al. 1978c.

Due to the high concentration of sulfuric acid and nitrosylsulfuric acid, corrosion is a serious problem. Currently either fluorocarbon-lined or Alloy 20 type material is used in the construction of equipment that will come in contact with this corrosive mixture (Farber 1976).

Sellite towers are not currently in use at Radford AAP; consequently, tetranitromethane is vented to the atmosphere. Analysis of air samples taken at various points in the manufacture of TNT by the Radford process is shown in Table 5.1. It is noteworthy that maximum tetranitromethane emission occurs during the acid wash and maximum NO_x emission occurs in separator 2 and nitrator 3.

5.2 SULFER DIOXIDE AND SULFURIC ACID MIST

A major source for emission of SO_2 and sulfuric acid mist in the AAPs is the sulfuric acid regeneration plant (see Section 3.8). The emission rates shown in Table 5.2 are for the Volunteer AAP sulfuric acid recovery unit operated at 71.5 to 94.3 percent capacity. The sources of emissions are noted below, together with controls and appropriate measuring points (Carpenter et al. 1978c):

Sources	Controls	Appropriate Emission Measuring Points
SO_2 from incomplete conversion of SO_2 to SO_3	Sellite tower	Exit stack from sellite tower
H_2SO_4 mist generated in absorption towers	Mist eliminators	Exit stack from sellite tower

The emissions in Table 5.2 are well below the Virginia Air Pollution Standard of 45 lb/ton of 100 percent sulfuric acid but slightly above the USEPA Performance Standards of 4 lb/ton (SO_2 emission) and 0.15 lb/ton (H_2SO_4 mist emission) of 100 percent sulfuric acid (see Section 11.2).

Novak (1983) pointed out that emission of NO_x and sulfuric acid mist from the batch TNT production lines and spent acid recovery units at Joliet AAP is a serious problem. At present these facilities do not have any pollution abatement control for these emissions.

TABLE 5.1. ANALYSIS OF AIR SAMPLES TAKEN AT 0600, SEPTEMBER 16, 1983, AT VARIOUS POINTS IN THE MANUFACTURE OF TNT BY RADFORD PROCESS[a]

Air sampling points (sources)	CO (%)	CO_2 (%)	TNM[b] (ppm)	NO (ppm)	NO_x (ppm)	O_2 (%)	N_2 (%)
Before AOP[c]	1.16	2.31	424	280	2595	15.91	61.60
After AOP	0.55	0.99	195	6.4	445	15.69	59.17
Nitrator 1	ND[d]	ND	60	15.5	23	20.73	77.28
Separator 1	ND	ND	18	100	285	19.97	75.28
Nitrator 2	0.12	0.53	18	4935	5945	19.09	75.90
Separator 2	Broken	–[e]	27	15,584	17,700	–	–
Nitrator 3	0.56	2.28	60	22,225	29,500	14.00	65.99
Separator 3	0.55	3.57	42	117	171	17.01	65.26
Nitrator 4	1.53	2.32	14	81.4	1799	17.48	65.63
Separator 4	0.31	0.87	<10	20	595	18.39	68.97
Nitrator 5	6.29	9.22	<10	24.5	1128	16.06	60.21
Separator 5	0.38	0.46	1	3	238	18.65	70.10
Nitrator 6	2.48	2.62	60	3.6	213	18.17	66.75
Separator 6	0.20	0.24	127	3.9	207	19.33	72.03
Nitrator 7	1.91	1.99	49	3.5	174	17.88	66.83
Separator 7	0.20	0.23	67	6.1	188	18.66	69.65
Nitrator 8	ND	0.08	18	3.3	86.1	20.70	77.20
Separator 8	ND	0.08	203	3.2	283	20.77	77.41
Acid wash	0.25	9.22	1032	19	2430	16.97	65.81
Sellite wash	ND	ND	109	3.2	234	17.66	65.94
Post sellite wash	ND	ND	–	3	95	19.79	73.73
Post sellite wash	ND	ND	–	3.5	159	19.22	71.61

a. Adapted from Stull (1984).

b. Tetranitromethane.

c. AOP = Absorption System Process.

d. ND = Not determined.

e. Indicates data not available.

TABLE 5.2. EMISSION RATES FOR THE VOLUNTEER AMMUNITION SULFURIC ACID RECOVERY PLANT[a]

Compound	Acid Production (ton/d)	Emissions (ppm)	(lb/ton H_2SO_4)
SO_2	414.6	244	5.06
H_2SO_4	414.6	-	1.45

a. Adapted from Carpenter et al. 1978c.

Because sulfur dioxide emissions are the major cause of acid rain, the subject has received a lot of attention in the news media (Shabecoff 1985a). Two detailed reviews of the technology available for abatement of SO_2 emission have been published by the Electric Power Research Institute (EPRI 1982a,b). The status of spray-dryer flue gas desulfurization and the DOWA process developed by the Dowa Mining Company of Japan are the subject matter of these two documents. The former process is based on the removal of SO_2 by neutralization with lime or limestone and soda ash. The latter is based on the use of basic aluminum sulfate and calcium carbonate and consists of three distinct steps.

Absorption: $Al_2(SO_4)_3 \cdot Al_2O_3 + 3SO_2 \text{ ----> } Al_2(SO_4)_3 \cdot Al_2(SO_3)_3$

Oxidation: $Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + 3/2O_2 \text{ ----> } Al_2(SO_4)_3 \cdot Al_2(SO_4)_3$

Neutralization: $Al_2(SO_4)_3 \cdot Al_2(SO_4)_3 + 3\ CaCO_3 + 6H_2O \text{ ----> }$

$$Al_2(SO_4)_3 \cdot Al_2O_3 + 3\ CaSO_4 \cdot 2H_2O + 3\ CO_2$$

The feasibility of adopting these processes in the AAPs to reduce the emissions of SO_2 seems worthy of exploration.

5.3 ORGANIC POLLUTANTS

Emission of organic vapors is possible from several sources in the AAPs. For example, during the manufacture and crystallization of RDX, a variety of organics escape into air (see Table 5.3) (Carpenter et al. 1978b). Some explosive nitrobodies are sufficiently volatile to cause air pollution. Novak (1983) has pointed out that during the drying and coating of ball powder at Badger AAP a certain amount of nitroglycerin escapes by evaporation. It then condenses in the stacks or spreads out on the roof of the manufacturing building, resulting in the potential for environmental pollution in addition to posing a immediate safety hazard. An R&D effort is needed to solve this problem.

TABLE 5.3. EMISSIONS SUMMARY FROM RDX MANUFACTURE AT HOLSTON AAP[a,b]

Compound			Emission Rate (lb/day)	Emission Rate (ton/year)
GROUP I.	EPA Criteria Pollutants			
	Particulates		14,749	2,692
	Sulfur oxides		16,969	3,097
	Carbon monoxide		12,197	2,226
	Nitrogen oxides[c]		64,526	11,776
	Nonmethane hydrocarbons		2,908	531
GROUP II.	Organics			
	Acetic acid		12,746	2,281
	Acetic anhydride		430	42
	Formic acid		141	26
	Isobutyl acetate		2	0.4
	n-Propyl acetate		1,134	207
	n-Propyl formate		320	58
	Methyl acetate		733	134
	Cyclohexanone		2,278	416
	Acetone		2,754	503
	Methyl ethyl ketone		6	1
	Methyl nitrate		1,558	284
	Nitromethane		30	5
	Methyl and dimethylamine		18	3
	Toluene		52	9
	Phenol		0.8	0.1
	Trace organics (butanol, propanol, methanol, methyl formate, formaldehyde)		10	2
		TOTAL	(21,746)	(3,969)
GROUP III.	Miscellaneous Species			
	Methane		1,955	357
	Hydrogen		418	76
	Carbon dioxide		2,250,000	410,625
	Ammonia		390	71
	Nitric acid		4,409	805
	Explosives (particulates)		2.3	0.4

a. Adapted from Carpenter et al. (1978b).

b. Assumes full mobilization 670,000 lb/d.

c. Calculated as NO_2.

6. WATER POLLUTION FROM AAPs

6.1 TNT ASSOCIATED

Wastewater discharges from AAPs contain several types of pollutants, including TNT, nitrogen species, sulfur, phosphates, munition degradation compounds, and solids. Some of these pollutants are not exclusive to AAP discharges but do significantly affect the environment associated with AAPs. Data concerning discharge characteristics are available for several AAPs and can be compared to recommended levels or standards. The USEPA (1976, 1979a) has recommended National Primary and Secondary Drinking Water Regulations for many of these pollutants, and these levels are shown in Table 6.1. Water quality criteria values have been proposed for many pollutants. In other cases research is being undertaken to develop values for many of the primary munition compounds. These criteria are given in Section 11.6.

TABLE 6.1. USEPA NATIONAL PRIMARY AND SECONDARY DRINKING WATER REGULATIONS[a]

Pollutant	Level
Arsenic	0.05 mg/L
Barium	1.0 mg/L
Cadmium	0.010 mg/L
Chloride	250 mg/L
Color	15 Color units
Copper	1 mg/L
Corrosivity	Noncorrosive
Faoming agents	0.5 mg/L
Iron	0.3 mg/L
Lead	0.05 mg/L
Manganese	0.05 mg/L
Mercury	0.05 mg/L
Nitrate (as N)	10.0 mg/L
Odor	3 Threshold odor number
pH	6.5-8.5
Selenium	0.01 mg/L
Silver	0.05 mg/L
Sulfate	250 mg/L
Total dissolved solids	500 mg/L
Zinc	5 mg/L

a. Adapted from USEPA 1976 and USEPA 1979a.

Effluent discharge data for Volunteer AAP are given by Sullivan et al. (1977) for the October to December period of 1974. As shown in Table 6.2, the nitrogen species, sulfates, and munitions that were discharged exceeded limitations set by the National Pollutant Discharge Elimination System (NPDES) of the USEPA. Discharges from AAPs also contain a variety of inorganic compounds (e.g., at Volunteer AAP, Table 6.3) that arise during manufacture and purification of TNT (Ribaudo et al. 1981). It is thought that heavy metals found in the effluent originate in the stainless steel reaction vessels and holding tanks and are leached out by the acid mixtures. Many of the discharged inorganic components, including copper and chromium (maximum values of 0.22 and 0.16 ppm, respectively), fail to comply with the Federal Environmental Pollution Standards and the Tennessee State Pollution Standards. Analysis of service water into the plant (copper, 0.01 ppm; chromium, not detected) indicates that these ions enter the discharge water within the plant. Because Volunteer AAP discharge water is alkaline, most of the metal salts hydrolyze and precipitate; but these metal hydroxides may be made water soluble by chelation with TNT or its degradation products and may be toxic.

TABLE 6.2. NPDES[a] DISCHARGE STANDARDS AND TYPICAL EFFLUENT DISCHARGE DATA FROM VOLUNTEER AAP[b]

Parameter	NPDES Limits mg/L/d		VAAP Monitoring Data			
			Quantity (lb/d)		Concentration (mg/L)	
	Average	Maximum	Minimum	Maximum	Minimum	Maximum
NH_3-N	0.1	0.5	6.9	140	0.21	3.5
BOD[c]	(66[d])	10	45	2,890	1.6	12.0
COD[e]	-	20	297	713	7.1	25.7
Dissolved solids	750	1,000	4,670	36,000	130	1,000
NO_2-NO_3-N	-	10	76	1,050	2.4	22.2
SO_4	-	250	2,020	15,000	40	300
Suspended solids	30	-	159	1,450	2.0	29.0
TNT + Nitrobodies	0.3	0.5	0	104	0	3.2

a. NPDES = National Pollutant Discharge Elimination System, USEPA.

b. Adapted from Sullivan et al. 1977.

c. BOD = biological oxygen demand.

d. Value is given in lb/day.

e. COD = chemical oxygen demand.

TABLE 6.3. RESULTS OF CHEMICAL ANALYSES OF DISCHARGED WATERS FROM THE VOLUNTEER AAP IN 1976a

Chemical or Parameter	Concentrations (ppm)					Regulations (mg/L)
	4/30	8/17	8/20b	9/03	9/25	EPA (State)
Aluminum	0.075	0.29	0.03	0.06	0.15	NGc
Arsenic	0.09	0.07	0.08	0.09	0.03	NG
Barium	0.017	0.05	0.02	0.02	0.06	NG
Bromine	0.06	0.18	0.99	0.06	0.29	NG
Calcium	0.52	47.5	430	69.5	47.5	NG
Cerium	NDd	ND	ND	ND	ND	NG
Cesium	0.27	0.02	0.06	0.01	0.07	NG
Chromium	0.09	0.16	0.10	0.11	0.12	0.05 (0.075)
Copper	0.01	0.22	0.16	0.09	0.05	0.02 (0.03)
Iron	0.27	0.03	0.01	0.03	0.02	0.3 (0.45)
Lanthanum	ND	ND	ND	ND	ND	NG
Lead	0.002	0.01	0.007	0.004	0.03	0.05 (0.075)
Magnesium	1.11	0.93	0.94	0.87	0.79	NG
Manganese	0.02	0.02	0.30	0.18	0.05	0.05 (0.075)
Nickel	0.12	0.11	0.22	0.13	0.12	NG
Nitrogen (total)	>11.0	>10.0	>50.0	>10.0	>10.0	NG (30)
Phosphorus	0.007	0.10	0.02	0.003	0.08	0.1 (0.15)
Potassium	4.2	0.82	0.73	0.43	0.72	NG
Silicon	16.6	2.3	1.90	3.3	3.4	NG
Sodium	12.2	138	55.2	32.3	34.9	NG
Strontium	ND	0.13	0.12	0.08	0.17	NG
Sulfur	47.5	42.7	48.0	43.0	38.8	NG
Vanadium	0.009	0.17	0.15	0.034	0.08	NG
Zinc	0.04	0.13	0.05	0.20	0.13	NG
Cl^-	13.	71.3	187.0	87.9	17.9	NG
Dis solidse	367.0	552.0	1197.0	410.0	334.0	1000 (750)
Dis solids/ HCl addedf	485.0	605.0	2071.0	888.0	330.0	NG
HCO_3^-	52.5	134.0	28.6	42.0	71.8	NG
NO_2^-	1.56	ND	ND	6.8	ND	NG
NO_3^-	21.0	27.0	295.0	4.6	62.0	NG
Organic N	1.12	0.56	0.70	0.84	1.12	NG
pH	7.90	8.18	7.32	7.60	7.75	6.5-8.5
Phenol	0.04	0.62	0.86	ND	1.95	0.001 (0.002)
SO_4^{-2}	63.6	204.0	995.0	151.0	101.0	250 (500)

a. Adapted from Ribaudo et al. 1981.

b. Composite of three days of samples.

c. NG = not given.

d. ND = not determined.

e. Dissolved solids.

f. Dissolved solids after the addition of hydrochloric acid (HCl) to the original water.

Information on the wastewater effluent of Radford AAP was also available. Luh and Szachta (1978) reported discharge values prior to treatment for areas of Radford AAP, depending on their manufacturing role (Table 6.4). As compared to EPA standards, the released pollutants exceeded acceptable levels. Although the data on munition compounds were incomplete at the time of their report, the data on nitrates indicate considerable release of munition-related nitrogen that exceeded the standards by a factor of 5. The authors did comment that installation of proposed treatment facilities would reduce the waste input to the aquatic system by 85 to 90 percent. Current reports from Radford indicate that treatment and operating procedures have met these goals for reducing nitrate emissions (see Section 8.21). Other data on the characterization of waste effluent discharges from Radford AAP were reported by Nay et al. (1974). They gave the average characteristics of continuous-flow TNT wastewater as containing 20 mg/L of alpha-TNT, 200 mg/L of nitrates (as N), 1000 mg/L of sulfates, 70 mg/L of chemical oxygen demand (COD), and 2000 mg/L of solids. These values represent the raw wastewater prior to the final treatment stages of neutralization and sedimentation.

Ghassemi et al. (1976) reviewed data on wastewater effluents from two earlier studies (1967 and 1972) of Joliet AAP. The data taken in 1967 indicated that the four main effluent streams discharged a daily total of 3.2 tons of nitrates, 72 tons of sulfates, 9.5 tons of COD, and 14.5 tons of suspended solids. These high levels were generated at a period of peak TNT production at Joliet AAP. The original report attributed much of the wastewater problem to equipment malfunction, operational errors, and lack of discipline in "housekeeping," resulting in spills to relatively clean cooling water. The 1972 study focused on the TNT manufacturing line 10, red water disposal, tetryl production, and sellite production. The TNT manufacturing line produced wastewater with average concentrations of 44 mg/L of suspended solids, 702 mg/L of dissolved solids, 16.5 mg/L of nitrates, 153 mg/L of sulfates, and 0.8 mg/L of TNT. The associated cooling waters were also found to contain 115 mg/L of sulfates and 33 mg/L of nitrates, indicating some leakage. The production of TNT generated about 1900 gallons of red water per batch, and the condensate resulting from the evaporation of this was found to contain high amounts of COD, nitrogen-containing compounds, and 20-22 mg/L of TNT. Sellite production contributed high concentrations of sulfite, sulfate, and total solids. At a flow rate of 0.173 MGD, the average values for these pollutants were 1340, 476, and 2096 lb/day respectively. The LAP area of Joliet AAP was also evaluated for contributions to the wastewater effluent. This pink water is generated by washing of shells and process equipment. On average, the pink water contained 1401 mg/L of total solids, 1265 mg/L of dissolved solids, 178 mg/L of TNT, and 145 mg/L of RDX. However, after treatment at a diatomaceous earth/carbon adsorption facility, the respective levels changed to 1070, 1072, 3.7, and 19, which were significant reductions for the munitions.

TABLE 6.4. SUMMARY OF WASTEWATER EFFLUENT DATA FROM RADFORD AAP[a]

Parameter (lb/d)	TNT Plant	Neutralization Pond
Average flow (MGD)[b]	4.32	0.1627
Nitrates (N)	540	88.9
USEPA standards	108	
Sulfates	3,960	2,940
USEPA standards	792	
Chemical oxygen demand	1,800	85.1
Total dissolved solids	29,160	5,580
USEPA standards		
Total solids	29,160	5,610
TNT		104

a. Adapted from Luh and Szachta 1978.

b. MGD = million gallons per day.

Other data on LAP wastewater were compiled by Spanggord et al. (1978). They sampled the effluents of various AAPs to determine TNT and RDX levels as well as their ratio. At Iowa AAP the TNT levels of posttreatment effluent ranged from <0.05 to 24.3 mg/L with a mean value of 1.32 mg/L and a TNT/RDX ratio of 0.55. At Milan AAP, the TNT levels ranged from <0.05 to 210 mg/L with a mean of 20.0 and a TNT/RDX ratio of 1.02. The much higher values at Milan were due in part to a lack of treatment because the samples were taken at a sump location.

As with other LAP or pink water, treatment methods of diatomaceous earth filters and carbon adsorption columns at Iowa AAP have proved to be effective for removal of TNT and RDX from wastewaters (Table 6.5) (Jackson and Lachowski 1984). However, this technique does create a solid waste disposal problem, because the contaminated activated carbon must be either burned or landfilled. Similar results for removal of TNT were found for pink water treatment at Lone Star AAP (Table 6.6) (Patel et al. 1983).

TABLE 6.5. EFFECTIVENESS OF TECHNIQUES FOR REMOVAL OF WASTE MUNITIONS FROM PINK WATER AT IOWA AAP[a]

Pink Water Sample Location	TNT (mg/L)	RDX (mg/L)	TOC[b] (mg/L)
Untreated from settling tank	109.4	8.5	60.3
After diatomaceous earth filter	88.1	8.5	52.7
After first carbon adsorption column	0.7	0.3	13.9
After second carbon adsorption column	0.3	0.0	10.9

a. Adapted from Jackson and Lachowski 1984.

b. TOC = total organic carbon.

TABLE 6.6. POLLUTION ABATED WASTEWATER CHARACTERISTICS AT INDUSTRIAL WASTEWATER TREATMENT PLANTS AT LONE STAR AAP[a]

Parameter (mg/L)	C-141 TP[b]		0-47 TP[b]	
	Inlet	Discharge	Inlet	Discharge
pH	7.24	7.28	7.09	7.59
Total solids	153	149	126	77
TSS[c]	7	27	12	23
N, ammonia	1.53	3.08	2.56	2.73
COD[d]	66	44	71	50
TNT	11.41[e]	0.02	16.01[e]	1.51
RDX	15.74	<0.10	15.29	0.83

a. Adapted from Patel et al. 1983.

b. Pink water treatment plant (TP) for area building C-141 or 0-47, consisting primarily of diatomaceous earth filter and carbon adsorption.

c. TSS = total suspended solids.

d. COD = chemical oxygen demand.

e. These levels are unrealistically low, due to dilution by rainwater. During actual melt pour operations, the values would be on the order of 100 to 300 mg/L.

Without some kind of waste treatment, the effluent discharged from AAPs will contribute a large amount of TNT and munitions-related pollutants into aquatic systems. However, the type of treatment employed may merely displace the direction of munition waste input from aquatic to atmospheric or terrestrial and create equally deleterious effects in those areas (see Section 9).

6.2 RDX AND HMX ASSOCIATED

RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) almost always occur together in AAP discharge wastewater. The association of ,RDX and HMX in wastewaters results from HMX being a contaminant of RDX manufacture and from their sharing a common manufacturing process (Sullivan et al. 1979).

Samples of the effluent wastewater from Holston AAP, the only plant producing RDX or HMX, were taken in May 1979 and reported by Stidham (1979). The four 24-hour samples of sample mass and flow rates taken from the manufacturing-waste effluent lines were used in calculating the averages of compounds delivered to the river. Values were calculated for the two main munition compounds and for the two principal by-products, 1-acetylhexahydro-3,5-dinitro-1,3,5-triazine (TAX) and 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX). The daily averages were 156 lb of RDX, 45 lb of HMX, 49 lb of TAX, and 33 lb of SEX. The concentrations, in mg/L, ranged from 0.110 to 16.02 for RDX and 0.090 to 3.36 for HMX. Maximum concentrations of 5.24 and 2.03 mg/L were recorded for TAX and SEX, respectively.

As with the discharges from TNT-producing plants, the effluents from Holston AAP contained inorganic pollutants traceable to the reaction and holding vessels (Chen et al. 1981). These pollutants included anions and cations (Table 6.7) as well as the heavy metals, cadmium, copper, and chromium (Table 6.8). These inorganic pollutants are important not only because of their basic toxicity, but also because of the potential for synergistic or additive interactions with organic components.

Data on RDX levels in the effluents from LAP sites in various AAPs were compiled by Spanggord et al. (1978). At Iowa AAP, LAP water contained 23.8 to 173 mg/L of RDX, with a mean of 80.5 mg/L, prior to carbon column treatment. After passing through the column, RDX content dropped to <0.1 to 24.4 mg/L with a mean of 1.53 mg/L. At Milan AAP, LAP water is sent to a sump and overflows to a stream. RDX concentrations at the stream ranged from 0.1 to 109 mg/L with a mean of 11.9 mg/L. Two other AAPs also use sumps but combine them with waste lagoons. Louisiana and Lone Star AAP data were given for these areas and had RDX concentration ranges of 6 to 189 mg/L and 5 to 82 mg/L, respectively. The reported values for these last three AAPs may be a little low because of production stoppages and dilution in the lagoons.

TABLE 6.7. INORGANIC IONS FOUND IN THE WASTEWATERS OF HOLSTON AAP FROM RDX AND HMX MANUFACTURE[a]

Ions	Concentration (ppm)			
	WW1[b]	WW2[c]	WW3[d]	WW4[e]
Na^+	21.0	20.9	16.5	16.7
NH_4^+	0.5[f]	2.0	0.2[f]	0.2
K^+	2.0	2.5	2.0	1.7
Cl^-	--	--	20.4	11.1
SO_4^{-2}	71.8	72.2	53.4	43.0
NO_3^-				16.6

a. Adapted from Chen et al. 1981.

b. Wastewaters from RDX manufacture.

c. Wastewaters from HMX manufacture.

d. Composite samples of wastewaters from RDX and HMX manufacture.

e. Value is an approximation.

TABLE 6.8. CADMIUM, COPPER, AND CHROMIUM FOUND IN HOLSTON AAP WASTEWATERS FROM RDX AND HMX MANUFACTURE[a]

Ions		Sample (ppb)			
		WW1[b]	WW2[c]	WW3[d]	WW4[e]
Cd	Average (6)	0.866	0.320	0.210	0.338
	Std. dev.	0.019	0.023	0.024	0.019
	Rel. std. dev.	2.2%	7.1%	11.2%	5.6%
	Rel. error	+2.1%	-	-10%	-5.4%
Cu	Average (6)	12.9	10.6	8.6	10.7
	Std. dev.	0.61	0.56	0.30	0.76
	Rel. std. dev.	4.7%	5.2%	3.5%	7.1%
	Rel. error	-3.1%	+11%	-	+11%
Cr	Average (6)	0.019	0.021	0.015	0.017
	Std. dev.	0.00096	0.00076	0.00088	0.0011
	Rel. std. dev.	5.1%	3.6%	5.9%	6.5%
	Rel. error	-	-	-	-

a. Adapted from Chen et al. 1981.

b. Wastewaters from RDX manufacture.

c. Wastewaters from HMX manufacture.

d. Composite samples of wastewaters from RDX and HMX manufacture.

Kitchens et al. (1978) reported data from Holston AAP for the amounts of RDX and HMX discharged per day at various operating conditions. They estimated that at full mobilization, minimum values for discharged munitions would be 340 lb RDX per day and 123 lb HMX per day. They also reported values for effluents at several internal sampling points and in the river for RDX, HMX, TAX, and SEX. The average values ranged from 0.01 (river) to 5.5 mg/L for RDX, 0.01 (river) to 2.6 mg/L for HMX, 0.004 (river) to 4.8 mg/L for TAX, and 0 (river) to 2.3 mg/L for SEX.

Solubility data for RDX and HMX (7.6 mg/L at 25°C and 0.14 g/L at 83°C, respectively) indicate that much of the compound concentration detected in the above water samples would be undissolved particulates.

The data cited above indicate the composition of the wastewater effluent discharged from RDX and HMX munition manufacture at Holston AAP prior to the most recent pollution control measures. Table 6.9 gives data for the current effluent discharged from the new Holston AAP wastewater treatment plant that went online in November 1983. Although munition levels are not given in Table 6.9, pilot studies have indicated that it is unrealistic to expect all of the RDX or HMX to be removed by nontertiary waste treatment facilities (Hash et al. 1977). The statement of Hash et al. is supported by personal communication from Evans (1984) that levels of 0.5 to 1 ppm of RDX/HMX (as well as by-products SEX and TAX) are released from Holston AAP. Currently, research efforts are being conducted by the US Army, based on the methodology of the USEPA (Stephan 1985), to generate water quality criteria values for RDX and some other munition compounds that will provide some guidelines for evaluating the impact of these reduced levels from Holston AAP (Etnier 1985). Of the pollution parameters given in Table 6.9, the maximum values for biological oxygen demand and total phosphorus were above NPDES permit levels for December 1983, and maximum values for total suspended solids, total nitrogen, total phosphorus, and ammonia (as N) were above NPDES permit levels for February 1984. Other parameters observed to exceed NPDES water standards at other sampling periods include chromium and copper (Evans 1984, pers. comm.). In all cases of exceeding permit values, the violations occurred for the maximum allowable levels.

Heffinger and Pregun (1985), examined Radford AAP waste treatment facilities for the ability to degrade RDX and HMX because it is planned that blending of nitramine propellants would be done at Radford. They evaluated the current Radford system (eight aerobic rotating biological contactors, operating in two parallel lines) by running a bench-scale rotating biological contactor for one month. They found that the system would not be capable of degrading RDX or HMX. This system is in contrast with Holston APP's waste treatment which consists of an anoxic tower, a trickling filter, and an

TABLE 6.9. CHARACTERISTICS OF HOLSTON AAP WASTEWATER TREATMENT EFFLUENTa

Parameter	NPDES Levelsb		March 1984		February 1984		January 1984		December 1983	
	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
BODc										
lb/d	1215	2430	85	697	161	1386	156	884	794	2682
mg/L	-	-	2	15	3.8	36	4.2	22	22	66
pH	6.0	9.0	7.4	8.1	7.6	8.0	7.0	8.0	7.4	7.9
TSSd										
lb/d	500	1000	127	419	346	5236	145	313	195	852
mg/L	-	-	3.0	10	8.2	136	3.6	7	5	22
SSe										
mg/L	0.5	0.5	0	0	-	-	-	-	-	-
Total N										
lb/d	600	780	83	356	157	912	94	380	156	769
mg/L	-	-	1.9	8.1	3.7	23.7	2.3	9.5	4	19
N, ammonia										
lb/d	200	300	4.2	64	72	634	0.7	11	28	177
mg/L	-	-	0.1	1.5	1.8	16.5	0.02	0.28	0.6	3.9
Total P										
lb/d	213	213	24	123	33	245	8	74	80	1237
mg/L	-	-	0.5	2.8	0.7	5.2	0.2	1.7	1.7	27.8
Total Cr										
mg/L	0.5	0.5	<0.01	<0.01	-	-	-	-	-	-
Total Cu										
mg/L	0.05	0.10	<0.01	<0.01	-	-	-	-	-	-
Total Pb										
mg/L	0.05	0.05	<0.01	<0.01	-	-	-	-	-	-
Total phenolics										
lb/d	10	20	0	0	0.04	0.4	0.1	1	0	0
mg/L	-	-	0	0	Tf	0.01	0.002	0.05	0	0
Flow, MGD	-	-	5.174	6.018	5.376	7.545	4.967	5.367	5.104	6.706
TDSg										
lb/d	600,000	600,000	3723	3723	-	-	-	-	-	-
mg/L	-	-	78	78	-	-	-	-	-	-
Total Hg										
mg/L	0.005	0.005	<0.001	<0.001	-	-	-	-	-	-

a. Data taken from NPDES discharge monitoring reports provided by J. Evans of Holston AAP.

b. National Pollution Discharge Elimination System permit levels.

c. BOD = 5-day biological oxygen demand.

d. TSS = total suspended solids.

e. SS = settleable solids.

f. T = trace amounts.

g. TDS = total dissolved solids.

activated sludge operation (Hash et al. 1977). In pilot studies of this system, analysis of effluent and inlet levels of RDX and HMX indicates that the anoxic tower alone removed 64.7 percent of RDX and 5.4 percent of HMX at flow of 0.8 gpm and 44.1 percent of RDX and 44.7 percent of HMX at flow of 1.2 gpm (Hash et al. 1977). Thus, neither system is highly efficient at removing these munitions from the wastewater effluents.

6.3 NITROCELLULOSE ASSOCIATED

Wastewater effluents from nitrocellulose manufacturing and alcohol rectification areas are characterized by high levels of solids and nitrates (Table 6.10). Early surveys of Badger and Radford AAPs indicated that nitrocelllose was present in plant effluents and was discharged to the environment (Cooper et al. 1975; Luh and Szachta 1978). Because of the centrifuge separation system and other pollution controls, levels comparable to those in Table 6.10 are no longer discharged to the environment from Radford AAP, although some nitrocellulose is still released in plant effluents (Smith 1984, pers. comm.). The amounts of released nitrocellulose should be below the proposed water quality criteria values designed to protect aquatic life and human health (Ryon 1985). Due to low toxicity of nitrocellulose, the criteria for control should be that concentration of nitrocellulose (as suspended and dissolved solids) that will not lower the compensation point of photosynthetic activity by more than 10 percent (USEPA 1976).

6.4 NITROGLYCERIN ASSOCIATED

Nitroglycerin has been found in wastewater effluents originating in manufacturing processes at Radford AAP (Tables 6.11 and 6.12). Other pollutants in these wastewaters are found in levels that exceed the Ammunition Procurement and Supply Agency (APSA) guideline values, used during the late 1970s, and include dissolved solids, total organic carbon, and filtered chemical oxygen demand. Pilot studies have indicated that various waste treatment operations could successfully reduce levels of nitroglycerin and associated pollutants in wastewater effluents before release to the environment (Table 6.13). Currently, the wastewaters from nitroglycerin and nitrate ester manufacture are being pretreated (to decompose the explosive compounds) and then combined with wastewaters from the propellant manufacture before being treated biologically. As with nitrocellulose and RDX, research and an evaluation are being sponsored by the US Army to generate water quality criteria values for nitroglycerine to provide protection of aquatic organisms and human health (Smith 1985).

TABLE 6.10. WASTEWATER CHARACTERISTICS FROM ASSOCIATED AQUATIC SYSTEMS AT BADGER AAP[a]

Pollutant/ Characteristic (mg/L)	Sampling Sites						
	ITP[b]	SL-1[c]	RP-2[d]	SL-3[e]	GBT-1[f]	WRT-3[g]	OC[h]
Nitrocellulose	10	3	6	5	7	<1	<1
Conductivity	370	960	360	710	800	220	100
Hardness	116	460	–	436	356	96	64
Suspended solids	24	24	–	12	<10	<10	44
Dissolved solids	230	874	–	810	566	68	26
Total solids	254	898	–	822	566	68	70
COD[i]	12	21	–	17	34	30	13
TOC[j]	11	12	–	10	13	12	8
NO_2	0.4	4.9	–	3.6	6.6	<0.1	<0.1
NO_3	4.8	125	–	125	25.1	0.1	2.2

a. Adapted from Cooper et al. 1975.

b. ITP = industrial waste treatment plant outfall.

c. SL-1 = head of settling lake below ITP outfall.

d. RP-2 = rocket pond effluent below nitrocellulose and nitroglycerin production areas.

e. SL-2 = base of third settling lake below ITP outfall and RP-2 outfall.

f. GBT-1 = transect across Greuber's Bay below ITP outfall and RP-2 outfall.

g. WRT-3 = partial transect in Wisconsin River below Badger AAP.

h. OC = Otter Creek, reference site not associated with Badger AAP.

i. COD = chemical oxygen demand.

j. TOC = total organic carbon.

TABLE 6.11. NITROGLYCERIN NO. 2 WASTEWATER AND COOLING WATER PRIOR TO TREATMENT OR DISCHARGE AT RADFORD AAP[a]

Parameter	mg/L		lb/d		APSA Effluent Guideline
	Mean	Maximum	Mean	Maximum	
pH units	9.4	9.9	-	-	6.0-8.5
Total solids	8,150	25,380	3,640	14,950	-
Suspended solids	6.4	39.0	2.9	22.9	25
Dissolved solids	8,143	25,351	3,630	14,900	500
Color	19.0	80.0	-	-	3-30
Total organic carbon	86.0	420.0	38.4	247.0	30
Filtered COD	81.7	195.0	36.5	114.5	20
NO_2/NO_3	458.2	1,920	204.5	1,130	-
Sulfate	145.4	466.0	65.0	274.0	200
Nitroglycerin	105.7	315.0	47.3	185.5	-

a. Adapted from Pollution Abatement Review Report No. 96020.007 as cited in Luh and Szachta 1978.

TABLE 6.12. NITROGLYCERIN NO. 2 WASTEWATER CHARACTERISTICS FROM RADFORD AAP[a]

Parameter	Range (mg/L)	Average (mg/L)	CI[b]
pH	8.8-9.4	9.05	0.14
Chemical oxygen demand	98.0-813.0	537.7	162.5
Total organic carbon	50.0-650.0	333.3	748.8
Total solids	19,480-56,970	37,404	10,978
Suspended solids	2.0-416.0	79.5	87.2
Nitroglycerin	291.0-1,062.0	759.2	189.5

a. Adapted from Carnaham pers. comm., as cited in Luh and Szachta 1978.

b. CI = Plus/minus 95 percent confidence interval.

TABLE 6.13. NITROGLYCERIN NO. 2 WASTEWATER CHARACTERISTICS PRIOR TO AND FOLLOWING POLLUTION REMOVAL FROM PILOT PLANT WASTEWATER TREATMENT OPERATIONS[a]

Treatment Step	Parameter[b]	Concentration (mg/L)		Percentage Removal
		Influent	Effluent	
Denitration	COD	98-813	232-692	0-37.9
	TOC	50-650	145-275	0-57.8
	NG	291-1,062	0-59	up to 99.9[c]
Coagulation and sedimentation	COD	232-692	196-711	0-31
	SS	6,478-14,289	53-291	97.3-99.6
Carbon adsorption	COD	118-769	212-558	0-45.8

a. Adapted from Carnaham pers. comm., as cited in Luh and Szachta 1978.

b. COD = chemical oxygen demand; TOC = total organic carbon; NG = nitroglycerin; SS = suspended solids

c. Time dependent.

7. <u>SOLID WASTES FROM AAPs</u>

Solid wastes from AAPs include various types of materials. Spills of munition compounds or component chemicals during manufacture, transportation, and storage create a solid waste composed of explosives and contaminated soils. The settling on surface soils of airborne particles from manufacturing and open incineration creates a similar type of material.

Dumping of ashes from incineration and of explosive-contaminated material in a landfill creates a solid waste through a treatment method. Contaminated sediments from wastewater ditches and lagoons and sludge from waste treatment plants are major types of solid wastes from munition manufacture. A primary disposal method for solid wastes is dumping in sanitary landfills, either on site or at approved disposal locations. Because of the association with soils, much of the solid wastes from munition manufacturing may eventually enter groundwater. Due to these reasons and pressure from regulatory agencies, disposal by other means is being considered and implemented for certain munition sludges.

7.1 TNT ASSOCIATED

Data on levels of TNT munitions entering soils are not readily available in the literature. Most data concern levels detected in soils or groundwater after entry. Other information documents the existence of various routes of entry.

Jerger et al. (1976), in an environmental analysis of Iowa AAP, found an abandoned waste lagoon site that after 20 years of disuse had become terrestrial in nature. The lagoon had been allowed to naturally fill in, with the addition of fly ash and solid coal wastes from the onsite coal-fired generators. Levels of munition-associated wastes in the soil of this area were found as follows: 0.5 mg/kg of 2,6-dinitrotoluene, 3.0 mg/kg of 2,4-dinitrotoluene, 0.6 mg/kg of 1,3,5-trinitrobenzene, 3030 mg/kg of 2,4,6-TNT, 101 mg/kg of 4-hydroxylamino-2,6-dinitrotoluene, and 180 mg/kg of 2-hydroxylamino-4,6-dinitrotoluene. The physical nature of the site had also changed, with the ground being barren and a deep reddish color. Pereira et al. (1979) documented the contamination of groundwater below waste disposal beds at Hawthorne Naval Ammunition Depot by TNT at levels of up to 620 g/L.

Bender et al. (1977a) reported that the production area of Volunteer AAP has been contaminated by spills from transportation and manufacture of TNT. This includes the batch TNT lines, burning grounds, and the sanitary landfill. Also, fallout of particulates downwind from the production area was identified as a contamination route. Similar documentation of entry into soil and groundwater from production lines, disposal sites, and emission fallout is

given for Milan AAP by Envirodyne Engineers, Inc. (1980), and for Alabama AAP by Keirn et al. (1981).

Keirn et al. (1981) reported the levels of munitions found in the soil of Alabama AAP, a facility that produced munitions between 1942 and 1945 and was maintained in standby condition until 1973 (Table 7.1). The levels of various TNT-derived compounds were quite high in some localities. In particular, the former manufacturing areas and the landfill (at depth of 230 cm) contained high concentrations of TNT and many of its degradation products. When it is considered that the manufacture of TNT stopped at this site more than 30 years prior to sampling, the long-term problem of the solid waste generated by munitions production is indicated. The report also provided data on groundwater quality. The groundwater sampled at Alabama AAP did show some effects from the TNT production, including sizeable increases in levels of nitrate/nitrite-nitrogen and smaller increases in specific conductance and sulfates (Table 7.2). Two sites had elevated levels of munitions and munition decomposition products (Table 7.2) that were traced to production facilities.

The evaluation of Milan AAP included data on soil contamination by munitions and associated compounds (Envirodyne Engineers, Inc. 1980). Table 7.3 indicates the extent of the contamination and the degree with which it is associated with munition disposal areas. Levels were found for RDX up to 83 g/g and for TNT up to 25 g/g. The presence of large levels of RDX and TNT indicate that substantial amounts of the primary munitions have not undergone degradation. The groundwater of Milan AAP was also evaluated for effects on the water quality (Envirodyne Engineers, Inc. 1980). Samples taken from various wells on the site indicated selected areas of groundwater contamination with detectable levels of TNT, RDX, and their degradation products (Table 7.4). Levels of nitrates, nitrites, sulfate, and phosphate were found that exceeded normal groundwater levels, indicating a plume of contamination originating at surface storage lagoons (Table 7.4).

Waste ash from open burning of spent carbon was also a source of solid waste and was either left at the burning grounds or deposited in a landfill. Data from Crane AAP (Table 7.5) indicates that open burning leaves significant amounts of TNT (and other munition compounds) in the residual ash (Jackson and Lachowski 1984). For this reason as well as other regulatory restrictions on open burning of explosives, incineration of spent carbon waste is now generally restricted to fluidized beds or rotary kilns. The solid wastes from these processes are much less of a problem than those created by open burning (see Section 9.1).

7.2 RDX AND HMX ASSOCIATED

Routes of entry similar to those of TNT are expected for RDX and HMX munitions and wastes. The data on TNT contamination at Milan AAP generated by Envirodyne Engineers, Inc. (1980), are accompanied by some data on RDX contamination (Table 7.3). Bender et al. (1977b) found contamination of RDX and HMX

TABLE 7.1. SUMMARY OF MUNITION LEVELS IN SOILS AT ALABAMA AAAPa

Sample Location (Alabama AAP area)	Sample Depth (cm)	Number of Samples	2,4-DNTb (ppb)	2,6-DNTc (ppb)	TNT (ppb)	TNBd (ppb)	DNBe (ppb)
Magazine	10	2f	160	NDg	ND	1965	ND
Old burning ground	10	5	488	115	177	<369h	<170
Old burning ground	15	2	<112	<102	<37	<369	<170
Old burning ground	50	1	386	<102	<37	<369	<170
Old burning ground	100	1	766	471	90	<369	<170
Propellant shipping	10	1	370	ND	ND	ND	ND
Rifle powder finishing	10	10	1757	ND	ND	ND	ND
Leaseback area	10	5	825	ND	ND	ND	ND
Leaseback area	10	1	825	ND	ND	615	ND
Burn./Sanitary landfilli	10	3	<112	<102	<37	<368	<170
Burn./Sanitary landfill	100	1	<112	<102	<37	<368	<170
Burn./Sanitary landfill	230	1	<112	<102	1,170	1,530	<170
Southern TNT manufacturing	10	11	152	166	273,066	459	<170
Southern TNT manufacturing	100	1	793	4,840	120	<368	<170
Northern TNT manufacturing	10	7	1,105	134	101,433	713	191
Flashing ground	10	7	572	<102	396	875	<170
Flashing ground	25	1	<112	757	<37	684	<170
Flashing ground	90	1	<112	<102	79	<368	<170

a. Adapted from Keirn et al. 1981.

b. 2,4-DNT = 2,4-dinitrotoluene.

c. 2,6-DNT = 2,6-dinitrotoluene.

d. TNB = 1,3,5-trinitrobenzene.

e. DNB = 2,4-dinitrobenzene.

f. In samples of 2 or more, values are averages.

g. ND = not determined.

h. < Values represent the limit of detection for that munition; in averages, < numbers were assumed to be equal to the detection limit.

i. Landfill contains wastes from burning grounds and sanitary waste treatment facilities.

TABLE 7.2. SUMMARY OF GROUNDWATER QUALITY DATA AT ALABAMA AAPa

Sample Location[h]	Sp. Cond.[b] (μmho/cm)	pH	Nitrate/Nitrite (ppm as N)	Sulfate (ppm)	2,4-DNT[c] (ppb)	2,6-DNT[d] (ppb)	TNT[e] (ppb)	TNB[f] (ppb)	DNP[g] (ppb)
Background values	74-180	5.9-6.2	<0.1-3.23	<7-23					
LBA, P-1	180	6.1	0.189	23	ND[i]	ND	ND	ND	ND
LBA, P-2	74	5.9	2.49	<7	ND	ND	ND	ND	ND
LBA, P-3	768	6.7	<0.10	41	ND	ND	ND	ND	ND
IND, P-4	33	6.1	0.408	<7	ND	ND	ND	ND	ND
IND, P-5	282	6.3	0.346	40	ND	ND	ND	ND	ND
IND, P-6	150	6.4	0.117	19	ND	ND	ND	ND	ND
IND, P-7	76	6.0	<0.100	8	ND	ND	ND	ND	ND
IND, P-8	384	6.7	<0.100	24	ND	ND	ND	ND	ND
IND, P-9	492	8.2	<0.100	25	ND	ND	ND	ND	ND
IND, P-10	354	5.4	25	29	4,340	860	10,270	4,380	1,100
IND, P-11	382	6.8	1.53	45	21	38.7	74.4	<5.3	ND
IND, P-12	232	6.2	0.891	<7	ND	ND	ND	ND	ND
IND, P-13	552	6.5	10.5	49	ND	ND	ND	ND	ND
IND, P-14	186	6.2	0.478	27	ND	ND	ND	ND	ND
IND, P-15	122	6.0	0.330	16	ND	ND	ND	ND	ND
IND, P-16	40	5.8	0.421	<7	ND	ND	ND	ND	ND
IND, P-17	389	6.3	<0.100	45	ND	ND	ND	ND	ND
IND, P-18	195	6.1	0.402	<7	ND	ND	ND	ND	ND
IND, P-19	236	6.2	1.10	61	ND	ND	ND	ND	ND
IND, P-20	50	5.6	0.238	<7	ND	ND	ND	ND	ND
GSA, P-21	77	6.0	0.116	<7	ND	ND	ND	ND	ND
GSA, P-22	120	6.2	<0.100	8	ND	ND	ND	ND	ND
GSA, P-23	93	6.0	0.116	<7	ND	ND	ND	ND	ND
IND, P-25	58	5.9	0.232	<7	ND	ND	ND	ND	ND
IND, P-26	133	6.0	0.284	<7	ND	ND	ND	ND	ND

a. Adapted from Keirn et al. 1980.

b. Sp. Cond. = specific conductance.

c. 2,4-DNT = 2,4-dinitrotoluene

d. 2,6-DNT = 2,6-dinitrotoluene.

e. TNT = 2,4,6-trinitrotoluene.

f. TNB = 1,3,5-trinitrobenzene.

g. DNP = 2,4-dinitrophenol.

h. Areas of AAAP in which wells were located, LBA = Leaseback area; IND = industrial area (explosives manufacture, flashing grounds, Manhattan Project area, sanitary landfill); GSA = General Services Administration area.

i. ND = not determined.

Table 7.3. SUMMARY OF MUNITION LEVELS IN SOILS AT MILAN AAPa

Sample Location (Milan AAP aread)	2,4-DNTb (ng/g)	2,6-DNTc (ng/g)	TNT (ng/g)	RDX (ng/g)	Nitrate (µg/g)	Nitrite (µg/g)	Phosphate (µg/g)	Sulfate (µg/g)
Background-1A	-e	<0.2f	<2	<60	1.7	0.50	<0.5	30
Background-1B	-	<0.2	<8	-	1.5	0.10	<0.5	35
Background-1C	-	<0.2	5	<60	1.6	0.05	<0.5	20
Background-1D	-	<0.5	11	-	3.0	0.03	<0.5	18
Background-1E	-	<0.2	27	-	4.5	<0.03	<0.5	20
Background-2A	-	<0.2	<2	120	1.9	1.2	<0.5	30
Background-2B	-	1.1	3.7	160	1.7	0.20	<0.5	30
Background-2C	-	<0.2	2	<60	1.4	0.38	<0.5	30
Background-2D	-	<0.5	<8	-	1.4	0.18	<0.5	18
Background-2E	-	0.1	1.6	51	0.5	0.08	<0.5	18
BG, downwind-3A	-	-	67	770	0.90	0.05	0.6	25
BG, downwind-3B	-	1.4	6	200	1.0	0.05	0.8	30
BG, downwind-3C	-	<0.2	46	850	0.90	0.05	0.8	58
BG, downwind-3D	-	-	2	110	1.0	0.03	<0.5	20
BG, downwind-3E	-	<0.2	11	820	0.80	0.03	0.8	30
Old burning area-4A	-	-	65	<120	0.40	<0.03	0.5	25
Old burning area-4B	-	-	2	90	0.30	<0.03	<0.5	32
Old burning area-4C	-	29	140	83,000	2.7	<0.03	<0.5	30
Old burning area-4D	-	-	-	<2,200	0.70	<0.03	<0.5	25
Old burning area-4E	-	<0.2	230	6,000	0.70	<0.03	0.58	<12
Demolition area-5A	3	<0.5	23	-	3.5	<0.03	4	35
Demolition area-5B	34	2.1	78	310	2.2	<0.02	<0.5	38
Demolition area-5C	17	4	590	740	3.7	0.03	<0.5	25
Burning area-6A	<30	<5	110	<2,200	9.0	0.03	<0.5	55
Burning area-6B	580	87	9,500	13,000	9.1	0.25	<0.5	50
Burning area-6C	10	2	4,000	-	4.0	0.03	<0.5	32
Burning area-6D	600	320	4,400	<220	5.0	0.03	0.8	42
Pine forest, BC-7A	-	0.2	<2	200	0.78	0.22	3.8	25
Pine forest, BC-7B	-	<0.2	3	<60	3.9	<0.03	6.1	25
Pine forest, BC-7C	-	0.5	2	74	1.3	0.05	7.6	25
Pine forest, BC-7D	-	0.6	2	<60	4.3	0.15	4.4	20
Pine forest, BC-7E	-	0.2	<2	80	1.5	0.7	3.6	30
Old landfill marsh-8A	-	0.2	11	1,600	0.18	0.22	0.6	18
Old landfill marsh-8B	-	<2	<20	<600	0.45	<0.03	0.8	30
Old landfill marsh-8C	-	0.03	3.5	640	0.18	0.12	<0.5	42
Old landfill marsh-8D	-	2	40	6,100	0.50	<0.03	0.7	44
Old landfill marsh-8E	-	<2	20	46,000	0.50	<0.03	0.5	63
Lagoon spoil bank-9A	270	120	25,000	<220	12	0.22	<0.5	62
Lagoon spoil bank-9B	34	8	12,000	72,000	22	0.32	<0.5	75
Old nitrate spill-10A	-	-	30	<600	0.42	<0.03	<0.5	25
Old nitrate spill-10B	<0.8	0.9	16	110	0.60	<0.03	0.5	18
Old nitrate spill-10C	<0.8	-	29	70	0.28	0.03	<0.5	18
Old nitrate spill-10D	-	0.3	10	70	0.42	<0.03	<0.5	12
Old nitrate spill-10E	-	<0.5	10	-	0.30	0.03	<0.5	12
Old fertilizer spill-11A	-	0.7	7	5,300	0.50	<0.03	<0.5	30
Old fertilizer spill-11B	-	-	-	-	0.90	0.25	<0.5	18
Old fertilizer spill-11C	-	<2	20	5,400	0.82	0.03	<0.5	12
Old fertilizer spill-11D	-	-	62	32,000	0.60	0.30	<0.5	20
Old fertilizer spill-11E	-	-	24	620	0.30	0.05	<0.5	20

a. Adapted from Envirodyne Engineers, Inc. 1980.

b. 2,4-DNT = 2,4-dinitrotoluene.

c. 2,6-DNT = 2,6-dinitrotoluene.

d. BG, Downwind = background area, downwind from burning facility; Pine Forest, BC = pine forest samples below bird colony.

e. - = represents the absence of that compound.

f. < Values represent the presence of the compound below the limit of detection for that parameter.

TABLE 7.4. SUMMARY OF GROUNDWATER QUALITY DATA AT MILAN AAP[a]

Parameter[b]	Total Samples	Number of Positive Samples	Range (μg/L)	Average[c] (μg/L)	Detection Limit (μg/L)
Nitrate	44	44	<100-26,000	2,586	<100
Nitrite	44	44	<10-100	21	<10
Phosphate	44	44	<200-1,500	323	<200
Sulfate	44	44	<4,600-140,000	14,672	<4,600
2,4-DNT	39	5	<10-70	22	<10
2,6-DNT	39	1	5		
2,4,6-TNT	39	4	<10-3000	823	<10
1,3,5-TNB	29	1	1,100		<200
RDX	39	4	<20-780	270	<20

a. Adapted from Envirodyne Engineers, Inc. 1980.

b. 2,4-DNT = 2,4-dinitrotoluene; 2,6-DNT = 2,6-dinitrotoluene; 1,3,5-TNB = 1,3,5-trinitrobenzene.

c. Average is calculated with < values assumed to be equal to the value itself.

TABLE 7.5. ANALYSIS OF WASTE ASH PILE OF OPEN BURNED SPENT CARBON FROM CRANE AAP[a]

Chemical (mg/L)	Sample 1 (0-5 ft)	Sample 2 (5-10 ft)	Sample 3 (10-15 ft)	Sample 4 (15-21 ft)	Sample 5 (21-24 ft)
Chromium	0.06	0.08	<0.05	<0.05	<0.05
Lead	9.5	300.0	6.4	31.0	0.26
TNT	21.9	1.8	1.0	0.2	0.9
RDX	26.5	6.2	13.3	0.9	3.9
HMX	0.8	0.7	1.1	0.8	0.8

a. Adapted from Jackson and Lachowski 1984.

manufacturing areas and disposal sites at Holston AAP which included occasional disposal of sewage treatment sludge and explosive-generated incineration ashes in landfills. This disposal was particularly hazardous because the landfill area was affected by sinkholes and subsidence, indicating that groundwater contamination is a distinct possibility.

The major solid waste problem associated with RDX/HMX production at AAPs is the sludge generated from waste treatment facilities. Brundege et al. (1982) mentioned the sludge composition generated from the spent acid regeneration phase of manufacturing RDX/HMX at Holston AAP and indicated that it consisted primarily of sodium nitrate and ammonium nitrate contaminated with small amounts of explosives and other impurities. The spent acid sludge is treated with sodium hydroxide to destroy the remnant explosives, a process that changes the sludge classification to nonhazardous waste sludge. Various alternative treatment techniques to handle the sludge generated at Holston AAP have been suggested by Brundege et al. (1982) and are discussed in Section 9. Additional sludge associated with Holston operations comes from the industrial wastewater treatment facility; this sludge is classified as a hazardous waste. Current sludge disposal methods for Holston AAP, the only AAP currently producing RDX and HMX, are given in Section 8.8.

Groundwater wells located near the various landfills and wastewater storage lagoons (including the Existing Fly Ash Landfill, the Existing Sanitary Landfill, the Closed Fly Ash Landfill, the Closed Sanitary Landfill, the Tar Pit, the Burning Ground, and the Nitric Acid Area Equalization Pond) on Holston AAP property are currently monitored on a quarterly basis. Also, the following areas were monitored during the early 1980s: the Area B Spill Pond, the A-1 Equalization Basin, the Area A Treatment Lagoon, and the Nitric Acid Spill Pond. When compared to National Interim Primary Drinking Water Regulation standards, only the standards for nitrite-nitrate, specific conductivity, and sulfates at the Nitric Acid Equilization Pond were exceeded for the period from September to October 1982 (Lund 1983d). This pond has since been closed and a new concrete basin constructed. When compared with the standards of National Secondary Drinking Water Regulation, which deals primarily with criteria based on aesthetic quality of the water, several parameters were found to be above suggested standards. These parameters included total dissolved solids at the Closed Fly Ash Landfill and Tar Pit during October 1983 (Lund 1984); total dissolved solids at the Tar Pit and New Sanitary Landfill during July and August 1983 (Lund 1983b); manganese levels at the New Sanitary Landfill during July and August 1983 (Lund 1983b); total dissolved solids at the Existing Fly Ash Landfill during May 1983 (Lund 1983c); iron and manganese at the Fly Ash Landfill during April 1983 (Lund 1983a); and total dissolved solids at the Tar Pit during April 1983 (Lund 1983a). None of the groundwater monitoring wells at Holston AAP have detected munition compounds or degradation products (Evans 1984, pers. comm.).

7.3 NITROCELLULOSE ASSOCIATED

Waste treatment methods at nitrocellulose manufacturing plants produce sludges that contain nitrocellulose fines. These sludges can occur from process-specific waste treatment facilities or from general plant-wide waste treatment facilities. Smith et al. (1983b) described the various waste sludges generated at Radford AAP, including those associated with nitrocellulose production (Table 7.6). Nitrocellulose fines accounted for 18 percent of sludge produced in treatment facilities associated with nitrocellulose manufacture (NG-1 and alcohol rectification areas). An evaluation of the environmental fate of nitrocellulose sludge deposited in a landfill was done using lysimeter columns filled with soil, sludge, or a mixture of both (Huibregste et al. 1976). These experiments indicate that fines did not leach out of containment, but degradation products, nitrate/nitrites and cyanides, did leach out at concentrations up to 13,000 and 20 mg/L, respectively (Huibregste et al. 1976).

7.4 NITROGLYCERIN ASSOCIATED

Data on sludge production from nitroglycerin manufacture are given by Smith et al. (1983b). Table 7.6 shows the various manufacturing areas of Radford AAP that are associated with nitroglycerin production. Unlike nitrocellulose, residual nitroglycerin was not specifically identified in sludge, and the totals represent sludges generated by several manufacturing areas; thus it is hard to determine the amount of sludge material directly related to nitroglycerin production. Present processes for nitroglycerin and nitrate ester wastewaters route the treatment stream through a biological treatment facility, and any sludge generated would be limited to that plant.

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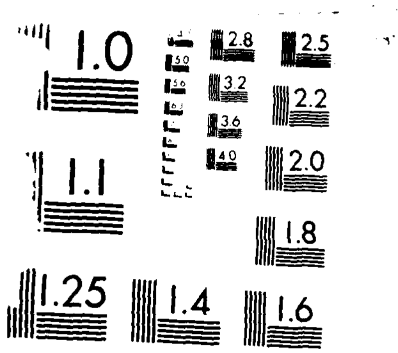

MICROCOPY RESOLUTION TEST CHART

TABLE 7.6. CHARACTERISTICS OF RADFORD AAP WASTEWATER TREATMENT SLUDGES[a]

Sludge Component	Quantity Produced[b] (lb/d dry weight)				
	NG-1/AR[c]	NG-2	SAR[d]	Biological	Total
Total sludge	3,564	4,915	37,749	1,080	47,308
Calcium sulfate	-	423	35,144	-	35,567
Calcium hydroxide	343	1,703	76	200	2,322
Calcium carbonate	1,422	2,262	-	-	3,684
Nitrocellulose	693	-	-	-	693
Lead	2.5	1.5	-	-	4
Iron	12.5	7.9	38	-	58.4
Others[e]	895	442	2,415	880	4,632
Magnesium	31	37	38	-	105
Sodium	32	19	-	-	51
Inorganic nitrates	109[f]	14	-	-	123
Silica	18.5	5.5	38	-	62
Cyanide	5.5[f]	-	-	-	5.5

a. Adapted from Smith et al. 1983b.

b. Values are for full mobilization production rates.

c. NG = nitroglycerin area; AR = alcohol rectification area.

d. SAR = sulfuric acid regeneration area.

e. Consists of CO_2, organics, and bound H_2O based upon their volatility at 825°C.

f. Cyanides and nitrates are present in aged sludge only, due to the decomposition of the nitrocellulose by the calcium hydroxide.

8. POLLUTION STATUS OF INDIVIDUAL AAPs

8.1 ALABAMA AAP

Alabama AAP is located in Childersburg, Alabama, and produced TNT, DNT, nitrocellulose, tetryl, and several types of powder formulations during its operation in the second World War. It is currently inactive and is undergoing decontamination in the nitrocellulose and powder production areas before being sold to a private firm (Wood et al. 1981). Surveys of the plant area have indicated soil, groundwater (Tables 7.1 and 7.2), and building contamination. Nitrocellulose is the major hazard in the buildings, and TNT and DNT are the major hazards in water and soils (Keirn et al. 1981). Because Alabama AAP is no longer a functioning production facility, pollution efforts will concentrate on installation restoration by removal of contaminated soils and building materials.

8.2 BADGER AAP

Badger AAP, located in Baraboo, Wisconsin, is another production facility that is currently inactive and has not operated since 1975; however, unlike Alabama AAP, it remains in the mobilization plans and may be reactivated in the future (USATHAMA 1984). Potential pollution problems include nitrocellulose and nitroglycerin production residues (Cooper et al. 1975) and the potential for pollution from future ball powder production (USATHAMA 1984). A survey performed in 1974 of the wastewater lagoons and associated aquatic systems of Badger AAP indicated that nitrocellulose was present in the sediments and water (Table 6.10) and would remain a pollution problem due to the slow , if any, physical degradation of nitrocellulose (Cooper et al. 1975). USATHAMA (1984) indicated that if production was resumed at the ball powder facility, additional pollution treatment facilities would be needed, because the existing facilities were incapable of meeting the newer environmental regulations. Research on appropriate treatment approaches has been scheduled for FY 1985-1986 (USATHAMA 1984).

8.3 CORNHUSKER AAP

Located in Grand Island, Nebraska, is another inactive AAP, Cornhusker AAP, although it is being maintained in a high state of readiness (Talmon et al. 1976). Cornhusker AAP is a LAP plant and if reactivated would need pollution treatment facilities to handle pink water, associated solid wastes, and air pollution resulting from the LAP activities. As of 1975, pollution treatment facilities included domestic sewage treatment plants and solid waste landfills; potential improvements included incinerators for contaminated and explosive wastes, air pollution monitors, and wastewater storage lagoons (Talmon et al. 1976). Current pollution abatement needs would require more extensive treatment of the pink water beyond lagoon storage if production was

resumed. A reevaluation of the long-term stability and security of landfill storage of solid wastes would also be advisable.

8.4 CRANE ARMY AMMUNITION ACTIVITY

Crane is a Naval facility located in Crane, Indiana, where Army Ammunition Activity is currently performed. Operations include LAP activity resulting in the formation of pink water, which is handled by carbon adsorption columns, settling tanks, and diatomaceous earth filters (Jackson and Lachowski 1984). At current production levels (noncontinuous flow and at a rate 50% of designed flow rate) the treatment of pink water is maximized. Sludge, including spent activated carbon, is disposed of by open burning, which is not totally satisfactory. Analysis of ash indicates that the munitions are not completely decomposed (Table 7.5). Also, the burning grounds and ash storage piles (representing over 40 years of ash accumulation) are located on a flood plain next to a stream and three evaporation pits (Andrews 1982). The potential for extensive water contamination from this site has prompted recommendations for the diversion of surface and runoff waters from Crane and development of plans to secure the ash storage piles (Andrews 1982). Environmental regulations will probably prompt a move to closed incineration of the waste sludge.

8.5 GATEWAY AAP

Gateway AAP located in St. Louis, Missouri, is inactive and is currently being disposed of by the General Services Administration as excess property.

8.6 HAWTHORNE AAP

Information on Hawthorne AAP is limited. It is located in Hawthorne, Nevada, and is currently on standby. It is a LAP facility handling RDX, HMX, and TNT but is also the western area demilitarization facility (Justus 1985, pers. comm.). Neither of these efforts is currently operational. Jackson and Lachowski (1984) mention it in a review of the LAP plants and their current pollution status. They indicate that Hawthorne is not currently producing pink water, has no discharge permit limits, and disposes of wastes by open burning. No indication is given that the carbon adsorption system of pink water treatment has been installed at the facility (Jackson and Lachowski 1984). Hawthorne is also listed as a Naval Ammunition Depot that operates as a demilitarization facility for conventional munitions (Shapira et al. 1978). Pereira et al. (1979) documented TNT contamination of groundwater below waste disposal beds at Hawthorne Naval Ammunition Depot at levels up to 620 g/L. Discussions with current staff at Hawthorne indicate that no NPDES permits are required because the only discharge is sanitary sewage which does not reach navigable water (Justus 1985, pers. comm.). A groundwater permit has recently been required by Nevada for the sanitary sewage treatment plant (an Imhoff tank discharging into an evaporation lagoon), and its approval is currently pending (Justus 1985, pers. comm.).

8.7 HAYES AAP

Hayes AAP is located in Pittsburgh, Pennsylvania, and is currently inactive in a standby mode. Pollution problems from Hayes AAP would be limited because only the metal casings are manufactured, and no munition compounds are processed.

8.8 HOLSTON AAP

Holston AAP is one of the primary munition production facilities currently operating and manufactures all of the RDX and HMX used by the Army. TNT is also handled at Holston as part of its LAP activities. Because of this important role in production, extensive pollution abatement controls have been installed at Holston. Wastewater effluents contained, at one time, high loads of munition compounds, nitrates, and other pollutants (Huff et al. 1975b). However, recent pollution abatement measures have reduced the pollution load from Holston. The primary improvement was the completion in November 1983 of a new wastewater treatment plant that effectively reduces the pollutants in the plant effluent by using settling tanks, earth filters, and biological treatment towers (Table 6.9) (Evans 1984, pers. comm.). Sludge and contaminated filter material generated from treatment of wastewaters are currently dewatered and shipped to an approved hazardous waste landfill site in Alabama. Because the current procedure has an associated annual cost of one million dollars, delisting and/or incineration techniques are being considered as alternative approaches (Evans 1984, pers. comm.). Solid waste problems are minimal, with the primary problem being potential groundwater contamination from landfills and open burning sites. Steps have been taken or are proposed for solving these problems, including changes in the structure and use of open-air burning pads (e.g., use of metal burning pans to limit any potential for migration of waste explosive) and a number of monitoring wells (Evans 1984, pers. comm.). Also the number of active on-site landfills has been reduced. Air pollution problems are limited, with open air burning of explosives and exceeding permit levels with start-up or shutdown operations being of primary concern. The following list contains several of the major problems remaining for pollution abatement at Holston and possible solutions as identified by Evans (1984, pers. comm.).

- The number one problem is disposal of waste explosives or explosive contaminated materials. These are now open-air burned on clay-lined pits, which are soon to be replaced by clay-lined pans that will be tied into the wastewater treatment system. [This step was completed in 1985 (Emerson 1985, pers. comm.).] Use of a rotary kiln or other incinerator is a possibility. The final choices or design requirements will be affected by regulatory standards scheduled to be set by USEPA in FY 1986.

- A clay holding pond designed to hold excess wastewater is scheduled to be converted to a concrete retaining structure. This should limit groundwater contamination. [This step was completed in March 1985 (Emerson 1985, pers. comm.).]

- The use of existing on-site sanitary, gas-tar, and fly ash landfills has been phased out with the solid waste being sent to new on-site state-approved landfills. [This step was completed in 1985 (Emerson 1985, pers. comm.).] Plans are also under way to locate possible sites on the Holston Reservation in case additional landfills become necessary.

- Waste tars are now burned in the steam plant instead of being landfilled. Monitoring programs have been initiated to determine if pollutants from these materials are escaping in the steam plant flue gases.

- The possibility of using activated carbon adsorption columns in the wastewater treatment is being considered, especially if water quality regulations require further reductions in the levels of RDX, HMX, or TNT. However, the average daily flow of 5 to 6 MGD makes this idea currently infeasible (Emerson 1985, pers. comm.).

- Possible recycling of plant wastewaters is also being considered. Such recycling would help reduce wastewater effluent discharged from the plant, might reduce total operating costs, and is an option built into the existing treatment facility.

- Filtration steps in the wastewater treatment can be a problem if rains or high operating rates increase total water flow through the treatment plant. Expansion of the plant to provide more capacity will be required in the future.

- Other problems relate to the possible full mobilization of all RDX/HMX lines at Holston. This would create m re wastes of all types, exceeding the limits of the treatment plant, and increase the potential for spills or leakage of wastes.

- Effluent streams of the ammonia recovery process used in RDX manufacture have been identified as containing a carcinogen, N-nitrosodimethylamine (USAEHA 1979). Various processes for removing this carcinogen, including ultraviolet/ozone decomposition or carbon adsorption, are discussed in the referenced study. Catalytic hydrogenation has also been studied and has shown the most positive results. A pilot plant will be constructed in 1985 to test this alternative (Emerson 1985, pers. comm.).

8.9 INDIANA AAP

Indiana AAP is located in Charlestown, Indiana, and was constructed in the 1940s. It is a LAP facility that formerly handled single- and double-based propellants for large artillery shells. Thus, the explosive compounds nitrocellulose and nitroglycerin are the principal explosive waste compounds.

Currently the six lines in the single-based LAP facility are on inactive standby, and the only activity is loading of propellant materials from Radford AAP into containers. No wastewater is created by this activity, and open burning of spilled propellants is performed in pans according to the latest Army guidelines. Due to this low activity the main pollutant problems at Indiana AAP are related to its prior production and contamination from improper disposal methods in the past. For example, the open burning grounds do contain contaminated wastes, and a small potential for groundwater contamination exists. If the main LAP lines were reactivated, then wastewater treatment facilities would need to be constructed, similar to the needed improvements at many of the other older AAPs.

8.10 IOWA AAP

Iowa AAP is a LAP facility located in Middletown, Iowa, that handles RDX, TNT, and tetryl munitions in its currently active operations. Surveys have indicated that contamination of surface water, groundwater, and sediments by munition compounds and waste products has occurred in the past (Weitzel et al. 1975; Jerger et al. 1976; Sanocki et al. 1976) and that some areas of plant property continue to have significant levels, especially in groundwater (Hammer 1982; Clear and Collins 1982). This contamination has been traced to prior disposal methods (e.g., lagoons), at least for some areas (Hammer 1982). Current wastewater treatment for pink water includes diatomaceous earth filters, carbon adsorption columns, and settling tanks (Jackson and Lachowski 1984). Such treatment has been shown to be quite effective (Table 6.5). Disposal of sludge from pink water treatment is by open-air burning (Jackson and Lachowski 1984). Lead sludges from detonator production are deposited in an on-site evaporation pond meeting Resources Conservation and Recovery Act specifications (Tatyrek 1983). Both of these methods should be considered temporary solutions, because lagoon storage just delays the need for detoxification of wastes, and open-air burning contributes to local air pollution. Incineration of wastes in a closed apparatus may be the eventual option for sludge disposal. A summary of the detonator waste effluents and standards is given in Table 8.1.

8.11 JOLIET AAP

Joliet AAP is a manufacturing plant for TNT and tetryl as well as a LAP facility handling various munitions. It is located in Joliet, Illinois, and is currently inactive and in a standby mode. Earlier surveys of Joliet indicated that large amounts of munitions (including TNT and RDX) were present in effluent streams and were being released to the environment (Ghassemi et al. 1976; Jerger et al. 1976; Stilwell et al. 1976). Current treatment methods include carbon adsorption for removal of munitions and nitrates from the pink and red water generated during operations (Helbert and Stull 1984, also see Section 6.1). When operational, emission of NO_x and sulfuric acid mist from the batch TNT production lines and spent acid recovery unit is a serious problem (Novak 1983). Currently, these facilities do not have any pollution abatement control for the emissions. For the long-term waste treatment needs

TABLE 8.1. DETONATOR WASTEWATER EFFLUENTS AND STANDARDS AT SEVERAL AAPs[a]

AAP	Flow, m^3/d (gal/d)		Present/Future NPDES[b] discharge limits	
	Peacetime	Surge/mobilization	Average (mg/L/d)	Maximum (mg/L/d)
Iowa	7.6 (2,000)	22.7 (6,000)	Lead: 0.1/NA[c]	0.15/NA
Kansas	14.4 (3,800		Lead: 1.0/0.01 RDX: 0.5/0.5 COD[d]: -/- Flow: 4,000/8,000 gal/day	1.5/0.15 1.0/1.0 NR[e]/200
Lone Star	6.5 (1,700)	349.1 (92,000)/(200,000)	Lead: No limits Antimony: 0.1/NA	 0.2/NA
Twin Cities	None	251.1 (66,330)	NR	NR
Lake City	18.45 (4,875)	58.25 (15,390)	Lead: 0.1/NA	0.15/NA

a. Adapted from Tatyrek 1983.

b. NPDES = National Pollution Discharge Elimination System.

c. NA = Not available.

d. COD = chemical oxygen demand.

e. NR = not regulated.

at Joliet, a closed-loop TNT purification process known as the Sonoco Sulfite Recovery Process (see Section 9.2) is being evaluated (Helbert and Stull 1984). If implemented at Joliet, this process would eliminate a majority of the water and air pollutants associated with TNT production; however, for full mobilization additional carbon columns for water treatment may be needed (Helbert and Stull 1984).

8.12 KANSAS AAP

Kansas AAP is a LAP facility located in Parsons, Kansas, and also produces detonators, although the current production is limited to two lines (Fischer et al. 1982). Earlier during periods of active conflicts, up to eight lines were operational. The characteristics of wastewater generated by the detonator activities at the plant are given in Table 8.2. A project assessing the effectiveness of several wastewater treatment techniques was performed at Kansas AAP, and the results of the techniques on limiting the levels of RDX in the effluents are given in Table 8.3. The recommendations of this study were to install an ultraviolet-ozonation system for wastewater from LAP areas 900, 1000, and 1100 to decontaminate the water for recycle and reuse within Kansas AAP (Fischer et al. 1983). This choice was based on effectiveness and economics; the filter and carbon column system was more effective but also more expensive. The authors also felt some of the LAP areas were not suitable for recycle efforts (Fischer et al. 1983). Jackson and Lachowski (1984) indicate that carbon adsorption and open-air burning of the resulting sludge are the current treatment methods used for the LAP areas of Kansas AAP. Tatyrek (1983) indicates that treatment for the detonator areas (including lead wastes) consists of desensitization by acetic acid or sodium hydroxide followed by discharge to local waters; this treatment did not meet EPA requirements. Based on a compliance schedule submitted to the EPA Region VII, permit levels of 200 mg/L/day for chemical oxygen demand (maximum) and 0.15 mg/L/day for total lead concentration (maximum) were established for the detonator areas on 1 July 1984. A summary of the detonator waste effluents and standards is given in Table 8.1.

8.13 LAKE CITY AAP

Lake City AAP is located at Independence, Missouri, and operates as a manufacturer of primer compounds and a LAP facility for small arms propellants (Cooper et al. 1975). Munition compounds handled at Lake City include nitrocellulose, RDX, trinitroresorcinol, lead azide, lead styphnate, tetracene, pentaerythritol, and mixtures of these compounds (Tatyrek 1983). Waste treatment consists of a water treatment plant to desensitize the primer compounds followed by a series of settling lagoons before release to local rivers (Cooper et al. 1975). A pilot plant study performed at Lake City demonstrated that carbon adsorption columns and earth filters could reduce munition compound levels, with TNT lowered from 100 to 0.01 mg/L and RDX lowered from 15 to 0.01 mg/L (Fischer et al. 1983). Studies were initiated to characterize fully the waste effluents (Butler 1981, as cited in Tatyrek 1983) and possible treatment methods (Deeley 1981, as cited in Tatyrek 1983).

TABLE 8.2. CHARACTERISTICS OF WASTEWATER EFFLUENT AT KANSAS ARMY AMMUNITION PLANT[a]

Building[b] number	RDX[c] (mg/L)	Lead (mg/L)	TSS[d] (mg/L)	COD[e] (mg/L)	pH	Wastewater/Shift (gal.)
701	ND[f]	0.67	0	1,879	12.6	210
704	-	5.5	0	136	12.2	58
705	-	360.0	0	136	13.1	972
707	ND	ND	0	1,879	8.0	58
712	ND	0.46	110	1,879	12.7	210
716	ND	78.0	9,400	1,130	12.6	210
717	ND	98.0	5,300	96.0	12.3	247
727	-	ND	40	6,067	7.0	21
729	0.05	7.5	330	1,879	12.0	21
732	-	199.0	11,700	6,067	12.5	99
737	-	0.55	0	136	11.2	58
738	-	0.31	0	136	9.9	58
740	-	9.9	50	136	11.0	231

a. Adapted from Tatyrek 1983.

b. Combined locations for COD analyses are: (1) 701, 707, 712, and 729 (2) 704, 705, 737, 738, and 740, (3) 727 and 732.

c. RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine.

d. TSS = total suspended solids.

e. COD = chemical oxygen demand.

f. ND = not determined.

8.14 LONE STAR AAP

Lone Star AAP is another LAP and detonator manufacturing facility that handles many types of munition compounds. It is located in Texarkana, Texas, and is currently active. A survey of the pollution status of Lone Star was made in 1976 and indicated that problems existed with water, air, and solid waste treatment and disposal (Griffin et al. 1976). The LAP area generates pink water containing munition wastes at levels of <0.10 to 114 mg/L for TNT and <0.10 to 112 mg/L for RDX at average flow rates of 0.005 to 0.025 MGD (Griffin et al. 1976). Treatment for this area consisted of baffle sumps with leaching pits and evaporation ponds. The leaching pits from the lead azide areas contained lead levels of 0.01 to 498 mg/L at average flow rates of 0.0005 to 0.021 MGD. Associated with these levels were pH values of 1.8 to 8.4 (Griffin et al. 1976). Air pollutants from munition activities were primarily smoke particulates from open-air burning of solid wastes. Remnants of

TABLE 8.3. EFFECTIVENESS OF WASTEWATER EFFLUENT TREATMENT AT KANSAS AAP[a]

Wastewater Treatment[b]	RDX Influent (mg/L)	RDX Effluent (mg/L)	Removal (%)	Wastewater Treated, L (gal)
UV (185 nm)	0.73	0.65	10.96	3463.7 (915)
	6.15	0.13	97.89	2552.2 (675)
	2.93	<0.10[c]	96.59	2552.2 (675)
	5.00	<0.10	98.0	4428.9 (1170)
UV (254 nm)	0.70	<0.10	85.71	3463.7 (915)
	8.00	0.30	96.25	3531.8 (930)
	10.80	0.80	92.59	2725.5 (720)
	15.30	2.30	84.97	2611.9 (690)
UV-03 (185 nm)	0.79	<0.10	87.34	4528.6 (1125)
	3.44	<0.10	97.09	1703.4 (450)
	12.22	<0.10	99.18	1188.6 (314)
	25.95	<0.10	99.61	1688.3 (446)
UV-03 (254 nm)	1.61	<0.10	93.79	605.7 (160)
	1.80	0.13	92.78	1059.9 (280)
	8.85	1.26	85.76	643.5 (170)
	13.55	0.74	94.54	757.1 (200)
EF-CC (1:1)	0.23	<0.10	56.52	4542.5 (1200)
	21.76	<0.10	99.54	4542.5 (1200)
EF-CC (1:2)	0.71	<0.10	85.92	22,712.5 (6000)
	5.45	<0.10	98.17	22,712.5 (6000)
	10.70	<0.10	99.07	18,927.1 (5000)
	25.36	<0.10	99.61	15,141.6 (4000)
	43.93	<0.10	99.77	18,927.1 (5000)

a. Adapted from Fischer et al. 1983.

b. Treatment methods include UV (ultraviolet photodecomposition) at specified wavelength, UV-03 (ultraviolet photodecompositon followed by ozone treatment), EF-CC (earth filter followed by carbon column adsorption) at specified ratios of filters to columns (e.g., 1:1).

c. Detection limit was 0.10 mg/L; percentage removed is based on 0.10 mg/L (worst case) in all instances where there was no detectable level of RDX.

solid wastes not burned, and nonexplosive contaminated solids are deposited in landfills. An evaluation of the potential for recycling water within the plant provided data on pink water treatment (Table 6.6) and lead azide detonator production wastes (Table 8.4). Treatment processes consist of settling tanks, filtration, and carbon adsorption for pink water treatment and pH adjustment, sedimentation, and carbon adsorption for the lead waste treatment (Patel et al. 1983). Sludge from treatment facilities is currently mixed with a kiln-dust by-product and shipped off-site for disposal in a landfill (Tatyrek 1983). Sludge characteristics are given in Table 8.5 (Tatyrek 1983). A summary of the detonator waste effluents and standards is given in Table 8.1.

8.15 LONGHORN AAP

Longhorn AAP is a LAP facility located in Marshall, Texas, and is currently active. Primarily, it handles materials for loading of pyrotechnic devices (e.g., for use in flares or smokes) with some storage of containerized munitions. The washdown water from the packing areas is stored temporarily in sumps and then trucked to an evaporative treatment facility. The solids (usually containing significant amounts of barium) are put in metal drums and shipped to a Defense Property Disposal Office facility. Open-air burning is also used to dispose of some wastes (Maley 1985, pers. comm.).

8.16 LOUISANA AAP

Louisiana AAP is an active LAP facility located in Shreveport, Louisiana. It uses nine carbon adsorption sytems to handle its pink water waste. Sludge disposal is by open-air burning, and the final wastewater effluent is held in tanks for reuse or discharge if munitions levels are below 2 mg/L (Jackson and Lachowski 1984).

8.17 McALESTER AAP

Located in McAlester, Oklahoma, McAlester AAP is a former Naval Ammunition Depot currently operated as an Army facility. It contains a LAP facility to handle TNT loading of Navy shells and was selected as the site for a new RDX/HMX manufacturing facility (Water and Air Research 1976a). Little information was available on current waste treatment, but expected treatment efficiency for the new facility is given in Table 8.6 (Water and Air Research 1976a). Jackson and Lachowski (1984) indicate that the only treatment system for pink water at McAlester AAP consists of a lagoon storage with open-air burning of solid wastes.

TABLE 8.4. CHARACTERISTICS OF PROCESS WASTEWATER FROM DETONATOR LINES AT LONE STAR AAP[a]

Parameter[b] (mg/L)	Area Buildings (process explosive)					
	Q-2 (lead styphnate)	Q-8 (NOL-130)	Q-10 (lead azide)	Q-20 (lead azide)	Q-23 (RDX[c])	Q-48 (multiples[d])
pH	12.37	11.98	1.39	1.47	7.24	11.25
Total solids	7158	7644	2215	2471	207	7094
N-nitrate	-	1025	-	-	-	813
COD[e]	18,763	59	5560	55	44	256
RDX	-	-	-	-	28.97	-
Chromium	<0.05	0.06	0.11	0.08	<0.05	<0.05
Lead	398	16.4	136	3.71	0.15	4.03
Nickel	0.11	0.08	0.07	0.08	<0.04	0.09
Zinc	0.718	0.162	0.526	0.207	0.137	0.150

a. Adapted from Patel et al. 1983.

b. All units are in mg/L, except pH, which is in standard units.

c. RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine.

d. Multiples = many explosives handled in this building.

e. COD = chemical oxygen demand.

TABLE 8.5. CHARACTERISTICS OF COMPOSITE SLUDGE[a] FROM LONE STAR AAP[b]

Parameter	Concentration (mg/L)
Aluminum	26.2
Arsenic	0.001
Barium	9.4
Calcium	271.0
Cadmium	0.30
Chromium	8.8
Iron	5190.0
Lead	630.0
Manganese	22.8
Mercury	0.004
Sodium	1,060.0
Zinc	56.0
Total solids	15,455
Total suspended solids	12,400
Volatile solids	2,315.0
Total organic carbon	120.0
Alkalinity (as $CaCO_3$ at pH 3.7)	2371
pH	7.8

a. Sludge results from wastewater treatment, is blended with cement by-products, allowed to solidify, and is finally disposed of at a commercial offsite landfill.

b. Adapted from Tatyrek 1983.

8.18 MILAN AAP

Milan AAP is an active LAP facility located in Milan, Tennessee, and also serves as a storage site for various types of ammunition. Munition compounds of TNT, DNT, RDX, HMX, and tetryl are handled as part of its operations (Copeland et al. 1983). As of 1976, six LAP lines were operating with three more on standby (Blaylock et al. 1976). Characteristics of wastewater effluents from Milan AAP include TNT levels of 1.0 to 1.5 mg/L, RDX levels of 0.58 to 2.20 mg/L, COD levels of 10 to 111 mg/L, and BOD levels of 4.9 to 260 mg/L (Blaylock et al. 1976). Air pollution from munition activities is limited to smoke particulates from open-air burning of contaminated wastes and excess explosives. An evaluation of the potential for water recycle at Milan AAP indicated several possible methods for treating pink water, including carbon adsorption columns and ultraviolet (UV) photodecomposition (Copeland et al. 1983). A unique approach for reducing water discharged from Milan was a suggestion to spray pink water onto land in buffer zones located within the

TABLE 8.6. POTENTIAL EFFLUENTS RESULTING FROM THE PROPOSED RDX/HMX FACILITY AT McALESTER AAP[a]

Parameter[b]	Process Waste Treatment[c]			Cooling Tower	Final Effluents[d]		
(mg/L)	Raw (1)	Minimum (2)	Design (3)	Blowdown (4)	(1+4)	(2+4)	(3+4)
Flow (MGD)	1.5	1.5	1.5	1.2	2.6	2.6	2.6
COD	1167	56	33	20	664	40	28
BOD	780	8.9	8.8	10	442	9.4	9.3
NO_3-N	198	5	3	2	112	4	2
TKN	74	3	-0.2	8	45	5	3
TDS	659	423	490	975	798	665	703
RDX	5	0.5	<0.01	<0.01	2.9	0.3	<0.01
HMX	1.4	0.5	<0.01	<0.01	0.8	0.3	<0.01
TNT	3.5	0.5	<0.01	<0.01	2.0	0.3	<0.01

a. Adapted from Water and Air Research 1976a.

b. COD = chemical oxygen demand, BOD = biological oxygen demand, TKN = total Kjeldahl nitrogen, TDS = total dissolved solids, RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine, HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, TNT = 2,4,6-trinitrotoluene.

c. Process water treatment: raw = untreated wastes, minimum = some treatment but not to design specifications, design = complete treatment as proposed in design specifications.

d. Effluents based on treatment levels as listed in prior columns.

plant. This would allow natural UV light (sunlight) to decompose the nitrobodies, followed by uptake and utilization by plants as sources of nutrients (Copeland et al. 1983). Jackson and Lachowski (1984) indicate that current wastewater treatment includes carbon adsorption columns and that open-air burning of solid wastes is still used.

8.19 MISSISSIPPI AAP

Mississippi AAP, located in Picayune, Mississippi, is a recently constructed metal shell fabrication and LAP facility, which is now in a low-production operational phase. The primary munition compounds that will be processed are RDX and Composition B, with two lines operating in the LAP area of the plant. Due to its recent construction, Mississippi AAP contains some advanced wastewater treatment facilities (including carbon adsorption columns for the LAP activity and filtration and precipitation for the metal areas) and is currently meeting most of the NPDES standards (Table 8.7), especially those dealing with explosive compounds (Matherly 1985, pers. comm.). However, to meet all of the RCRA and NPDES standards for full operation, some additional design modifications and improvements in operating procedures will have to be implemented based on the debugging and evaluation information gained during the current low-production operational phase.

8.20 NEWPORT AAP

Newport AAP is a TNT production facility with five production lines, located in Newport, Indiana. Newport AAP also serves as a storage site for toxic chemicals (Water and Air Research 1976b). It is currently on standby; only two of the lines have actually operated and then only one at a time (Weir et al. 1976). Characteristics of the TNT production discharge are given in Table 8.8 (Wa*er and Air Research 1976b). In addition to the pollutants from the TNT production line, other sources of pollution include the sulfuric acid regeneration plant (SAR), the ammonia oxidation plant (AOP), two nitric acid concentrating units (NAC), and two denitration units (DN) (Weir et al. 1976). As of 1976, treatment methods for the TNT waste included collection of red water from TNT areas followed by burning in rotary kilns. Ash cake (principally sodium sulfate) was taken from the kiln and stored in plastic-lined basins. Drainage from the basin was sent to a central pollution control center for neutralization with lime (Weir et al. 1976). Wastewater from the acid areas was also neutralized with lime at the pollution control center. An evaluation of possible methods for reducing sulfate pollution at Newport AAP recommended (1) the use of a two-stage water management technique to improve sulfate removal efficiency in the pollution control center, (2) the use of a lime pretreatment of well water and direct reuse of residue acid to reduce amount of sulfate generated, (3) replacement of lime in the pollution control center with barium hydroxide, and (4) the possible regeneration of lime from calcium sulfate or carbonate sludge for reuse rather than depositing the sludge in a landfill (Bane et al. 1977). Currently, a closed-loop purification process is being evaluated at Radford AAP for possible use at Newport.

TABLE 8.7. CHARACTERISTICS OF MISSISSIPPI AAP WASTEWATER TREATMENT EFFLUENTa

Siteb/ Parametersd	NPDES Levelsc		July 1985		August 1985		September 1985	
	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
IWTF:								
COD	75	125	40.0	49.2	39.65	64.2	51.93	71.5
pH	6.0e	9.0	6.0e	8.45	6.85e	8.61	6.07e	8.10
SS	30	45	4.4	12.0	3	5	4.5	10.0
Cyanide	0.04	-	0.012	0.015	0.019	0.023	0.006	0.013
Oil-grease	10.0	15.0	0.93	1.96	0.11	0.18	0.875	2.0
Total Al	3.0	5.0	0.36	0.53	0.34	0.62	0.26	0.32
Total Cr	0.05	-	0.02	0.03	0.03	0.05	0.003	0.001
Total Cu	0.10	0.15	0.05	0.07	0.05	0.07	0.03	0.03
Total Fe	1.0	1.5	0.22	0.26	0.31	0.43	0.24	0.28
Total Ni	0.10	0.15	0.06	0.10	0.06	0.09	0.02	0.03
Flow, MGD	-	-	0.148	0.204	0.1484	0.3087	0.1681	0.3205
SWTF:								
DO	5.0	-	2.26	4.38	6.55	7.85	6.5	7.6
BOD								
lb/d	31.3	46.9	1.83	3.53	1.94	6.05	2.125	4.83
mg/L	30	45	2.26	4.38	2.40	7.5	2.63	5.99
pH	6.0e	9.0	6.5e	7.7	6.93e	7.6	6.7e	7.6
SS								
lb/d	31.3	46.9	7.12	22.60	7.81	12.39	9.385	14.13
mg/L	30	45	10.8	28	9.67	15.35	11.625	17.5
Flow, MGD	-	-	0.0969f		0.0969f		0.0969f	
LAP WTF:								
pH	6.0e	9.0	6.50e	6.50	6.13e	6.42	6.60e	6.60
SSe	25	40	8.0	8.0	11.0	14.0	18.0	18.0
Oil-grease	10	15	3.5	3.5	7.55	11.7	0.0	0.0
Total nitrobodiesg	1.0	-	0.3	0.3	0.41	0.46	0.1	0.1

a. Data taken from NPDES discharge monitoring reports provided by D. Matherly (1985) of Mississippi AAP.

b. Sample sites: IWTF = industrial waste treatment facility; SWTF = sanitary waste treatment facility; LAP WTF = load, assemble, and pack waste treatment facility.

c. National Pollution Discharge Elimination System permit levels.

d. Parameters are given in mg/L unless specified otherwise. BOD = 5 day biological oxygen demand; SS = suspended solids; COD = chemical oxygen demand; DO = dissolved oxygen.

e. Values given are minimums rather than averages.

f. Flow is an estimate based on previous readings.

g. Nitrobodies include HMX, RDX, and TNT.

This process, the Sonoco Sulfite Recovery Process (SRP), will eliminate the need to landfill the ash cake from incineration of red water and help reduce the NO_x and SO_2 levels in flue gases (Helbert and Stull 1984). Application of this technology to Newport would require three SRP modules to handle full production levels, and, because a facility to manufacture sellite has already been built at Newport, construction of SRPs would generate excess Na_2SO_3 and require the sulfuric acid regenerators to be equipped with double gas absorption (Helbert and Stull 1984). Current NPDES permit levels for the various outfalls from Newport AAP are given in Table 8.9 (Morehead 1985, pers. comm.).

TABLE 8.8. CHARACTERISTICS OF TNT WASTEWATER DISCHARGED FROM NEWPORT AAP[a]

Parameter[b] (mg/L)	Number of Samples	Mean	Standard Deviation	Minimum	Maximum
Flow (MGD)	5	1.32	0.42	0.88	1.95
NO_3-N	32	106.6	59.4	3.0	215.0
NO_2-N	34	4.2	1.9	0.01	7.50
SO_4	34	1030	458	67	1850
Sodium	34	141.0	112.0	6.0	509.0
COD	34	23.0	18.0	0	55.0
TOC	32	22.9	15.0	1.6	73.0
TNT	34	2.5	2.4	0.2	8.0
TDS	34	2062	759	381	4018
TSS	34	8.7	8.7	0	40.0
pH	32	7.9	0.3	7.2	8.5

a. Adapted from Water and Air Research 1976b.

b. COD = chemical oxygen demand, TOC = total organic carbon, TNT = 2,4,6-trinitrotoluene, TDS = total dissolved solids, TSS total suspended solids.

8.21 RADFORD AAP

Radford AAP is perhaps the flagship of all AAPs in that it represents application of the most advanced pollution abatement and munition manufacture technology. Located in Radford, Virginia, it has the capabilities to manufacture TNT, nitrocellulose, nitroglycerin, oleum, a wide variety of propellants, and the various acids required in producing these munitions. Research on munitions production and associated pollution abatement techniques is also a part of the mission of Radford AAP. Therefore, many of the pollution problems occurring at Radford have been the focus of experimental approaches for pollution abatement, including those dealing with cost effectiveness and resource recovery and recycle (Hercules 1984a). Because of this leadership role, many surveys of pollution from Radford have been conducted (Huff et al. 1975a; Mayberry et al. 1976; Heffinger 1984).

TABLE 8.9. NPDES PERMIT LEVELS FOR WASTEWATERS FROM NEWPORT AAP[a]

Parameter[b]	Outfall[c] levels (mg/L)				
	SWTP 001	BR 101	TR 002	CWR 003	BAR 004
CBOD5	40 (40.5)[d]	–[e]	NR[f]	NR	–
COD	–	–	NR	NR	IM[g]
Chlorine	0.5–1.0	–	NR	NR	–
Flow	MGD	MGD	NR	NR	MGD
Nitrates	–	–	NR	NR	IM
Nitrobodies[h]	–	–	NR	NR	0.2
pH	6.0–9.0	6.0–9.0	NR	NR	6.0–9.0
TBOD5	CD	–	NR	NR	–
TDS	–	2,000	NR	NR	–
TSS	45 (48.6)	45	NR	NR	40

a. Data taken from National Pollution Discharge Elimination System (NPDES) permit application (September 10, 1985) provided by Morehead (1985) of Newport AAP.

b. Parmeters include TSS = total suspended solids; TDS = total dissolved solids; TBOD5 = total biochemical oxygen demand; CBOD5 = carbonaceous biochemical oxygen demand; COD = chemical oxygen demand.

c. Outfalls requiring permitting include: SWTP 001, which is the effluent main from the Sanitary Waste Treatment Plant; BR 101, which is the collected precipitation from the Red Water Ash Basin and Gypsum Settling Basin (detemined not to contain hazardous waste); TR 002, which contains untreated surface runoff from the TNT and acid manufacturing areas; CWR 003, which contains untreated surface runoff from the chemical warfare agent storage area and former production areas; BAR 004, which contains untreated surface runoff from TNT waste burning grounds.

d. Levels are monthly averages or, in cases of ranges, minimums and maximums; values in parenthesis are lb/d; flow rate is given million gallons per day (MGD).

e. Dash indicates parameter is not regulated on that outfall permit.

f. NR = not requlated, because of state decision not to require permits for storm runoff areas.

g. IM = initial monitoring for 6 months to determine whether significant quantities are being released, followed by a review of these requirements.

h. Nitrobodies include summation of TNT, 2,4-DNT, 2,6-DNT, HMX, and RDX concentrations.

i. CD = comparison data required monthly for one year from date of permit.

In the past, wastewater discharged from Radford contained various pollutants (e.g., see Table 6.4), and many treatment approaches were evaluated and implemented (Luh and Szachta 1978). Currently, wastewater streams contain acids, nitrobodies, solvents (such as ether, alcohol, and acetone), miscellaneous propellant ingredients, and excess thermal energy (Heffinger 1984). Treatment methods for these problems include acid neutralization using lime for waste from nitrocellulose and acid production, settling and recycle of wastes from nitrocellulose production, acid neutralization and tertiary treatment of TNT wastes, secondary treatment of domestic wastes (by trickling filters) and of solvents and propellant ingredients (by rotating biological contactors), and ash separation from power plant wastewaters (Heffinger 1984). Current research efforts to assist these control methods include alternative techniques to separate nitrocellulose fines from wastewater, improved separation techniques for removing solids from sulfuric acid regeneration water, and processes for improved red water treatment and recycle (Hercules 1984a; Helbert and Stull 1984). As a result of these efforts, the wastewater discharged from Radford contains few pollutants, rarely exceeds EPA standards, and has little impact on local aquatic habitats and organisms (Heffinger 1984). Table 8.10 shows the latest NPDES permit and pollutant levels for two major waste treatment effluents (Calli 1985, pers. comm.).

Solid wastes from Radford AAP include fly ashes from power plants, incinerators, and open burning grounds, sludges from settling and separation phases of wastewater treatment, and contaminated carbon from TNT wastewater treatment. Landfilling these wastes was the accepted means of disposal, but concern over groundwater contamination and long-term problems with landfill storage of toxic wastes have prompted research into alternative methods of sludge disposal (Smith et al. 1983). Included in this research is the possibility of decontamination and reuse of activated carbon used to remove nitrobodies from TNT wastewater. More extensive use of closed container incineration of solids wastes is also being investigated.

Air pollutants from Radford AAP include particulates from open air incineration of waste munitions and fumes released from munition manufacturing and waste treatment. New approaches to treatment of wastewaters (e.g., red water recycle and reuse of sellite) will also reduce amounts of fumes released to the atmosphere (Helbert and Stull 1984). Research investigating possible closed incineration of wastes, sludges, and contaminated carbon should also lead to a reduction of atmospheric pollutants (Hercules 1984a). Scrubbers or other smokestack filtering devices will help control problem fumes, such as tetranitromethane, that cannot be treated by other process changes (Helbert and Stull 1984; Smith 1984, pers. comm.).

TABLE 8.10. CHARACTERISTICS OF RADFORD AAP WASTEWATER TREATMENT EFFLUENT[a]

Parameter[b]	NPDES Levels[c]		August-September 1985	
	Average	Maximum	Average	Maximum
TNT WTP:[d]				
Flow (MGD)	-	-	2225	2851
pH	6.0[e]	9.0	6.4[e]	8.6
COD				
kg/d	400.0	700.0	243	267
mg/L	52.0	230.0	26	28
Sulfates				
kg/d	2400.0	6000.0	789	1071
mg/L	2100.0	2300.0	85	118
TNT/Nitrobodies				
kg/d	0.900	1.300	0.61	2.66
mg/L	0.500	0.7500	0.07	0.30
Temperature (°C)	-	32.00	-	33
Nitrogen, N				
kg/d	800.0	1600.0	283	338
mg/L	29.00	89.00	30.25	35.35
SWTP:				
Flow (MGD)	-	-	1296	1764
pH	6.0[e]	9.0	6.1[e]	7.9
BOD_5				
kg/d	1550.0	6300.0	1412	2575
mg/L	250.0	500.0	274	509
TSS (kg/d)	7500.0	12000.0	119	196
COD				
kg/d	4000.0	7500.0	2451	4048
mg/L	500.0	1000.0	487	800
Sulfates				
kg/d	3000.0	3600.0	100	124
mg/L	-	-	28.25	61.0
Nitrogen, N				
kg/d	-	-	0.66	1.42
mg/L	-	-	0.24	0.71
2,4-DNT				
kg/d	-	-	0	0
mg/L	-	-	0	0

a. Data taken from NPDES discharge monitoring reports provided by L. Calli (1985) of Radford AAP.

b. National Pollution Discharge Elimination System permit levels.

c. COD = chemical oxygen demand; BOD_5 = 5 day biological oxygen demand; TSS = total suspended solids.

d. Sample sites: TNT WTP = TNT activated carbon treatment plant; SWTP = biological sanitary waste treatment plant.

e. Values given are minimums rather than averages.

Because Radford represents the leading edge of pollution abatement at AAPs, many of the processes being implemented or tested at the plant will eventually be installed at other AAPs in the event of full mobilization. This pathway from testing and development at Radford to implementation and installation at other sites has previously led to the use of carbon columns and sludge incineration at other AAPs.

8.22 RAVENNA AAP

Ravenna AAP is a LAP plant that primarily processed large artillery shells and some mines. It is located in Ravenna, Ohio, and is currently inactive. Munition compounds handled at Ravenna included nitrocellulose, nitroglycerin, nitroguanadine, and TNT. Wastewater treatment facilities at the AAP utilize activated carbon columns to process pink water wastes, but if the plant was reactivated additional treatment facilities would be needed to handle the increased waste load.

8.23 RIVERBANK AAP

Riverbank AAP is inactive and is located in Riverbank, California. This AAP does not handle munition compounds and is involved only with the manufacture of metal shell casings.

8.24 SCRANTON AAP

Located in Scranton, Pennsylvania, this AAP is currently active. However, Scranton AAP is involved only with the manufacture of metal shell casings, and no munition compounds are loaded or processed.

8.25 ST. LOUIS AAP

St. Louis AAP, located in St. Louis, Missouri, is being maintained on a standby basis. It also manufactures only metal shell casings and does not process munition compounds.

8.26 SUNFLOWER AAP

Sunflower AAP, located in DeSoto, Kansas, has recently undergone modernization and has shifted from an inactive, standby state (Hercules 1984a) to active nitroguanadine manufacture. The new propellant manufacturing and supporting facilities for nitroguanadine production at Sunflower AAP incorporated research and development efforts to address pollution problems (USATHAMA 1984) and achieve regulatory compliance.

8.27 TWIN CITIES AAP

Twin Cities AAP is a small arms facility located in New Brighton, Minnesota, and is currently on standby, with operations similar to those of Lake City AAP (Tatyrek 1983). Wastewater characteristics are given in Table 8.11. Treatment methods include desensitization of munitions with steam, sodium hydroxide, and aluminum, followed by disposal in leach pits (Tatyrek 1983). The treated water is then discharged into the Arden Hills Metropolitan Wastewater Treatment Plant. A summary of the general detonator waste

TABLE 8.11. CHARACTERISTICS OF WASTEWATER DISCHARGED FROM TWIN CITIES AAP[a]

Parameter (mg/L)	Range[b]
Chemical oxygen demand	30 - 18,900
Total organic carbon	7 - 4,400
pH	7.0 - 12.9
Total solids	65 - 400,000
Sulfate	8,600 - 200,00
Sodium	1,070 - 16,000
Inorganic nitrogen	3 - 7,500
Organic nitrogen	180 - 2,300
Aluminum	7 - 3,400
Carbonate	500 - 5,700
Calcium	4,000 - 100,000
Lead	14 - 3,800
Sulfide	28 - 1,100
Antimony	7 - 3,000
Barium	7 - 5,500

a. Adapted from Tatyrek 1983.

b. At maximum waste flow of 66,330 gal/day (251.1 m^3/day).

effluents and standards is given in Table 8.1. No NPDES permit is required for Twin Cities because the discharge is to the metropolitan treatment plant (Oster 1985, pers. comm.). Table 8.12 lists the standards for the effluent discharged to the metropolitan treatment plant.

8.28 VOLUNTEER AAP

Volunteer AAP is a TNT production facility with six continuous manufacturing lines (one operational) and five batch manufacturing lines (to be used at full mobilization) (Hauze et al. 1977). It is located near Chattanooga, Tennessee and is currently operated on a standby basis. Wastewater from Volunteer AAP has been surveyed several times (Sullivan et al. 1977; Bender et al. 1977a; Huff et al. 1975c) and contained high levels of nitrogen species, sulfates, munitions (Table 6.2), and heavy metals (Table 6.3). Other pollutants found to exceed EPA permit requirements include phosphorus, biological oxygen demand, chemical oxygen demand, dissolved solids, and pH (Hauze et al. 1977). When the surveys were taken, treatment of munition wastes consisted of settling, neutralization, and storage ponds (Hauze et al. 1977). A sewage treatment facility was scheduled for completion in FY 1978 to assist in reducing water pollution (Bender et al. 1977a), and implementation of the red water recycle process using sellite has been proposed (Helbert and Stull 1984). Solid wastes from Volunteer AAP are similar to those of other AAPs. As of 1977, munition-contaminated wastes and red water were burned in open-air pits, and noncontaminated wastes were landfilled (Hauze et al. 1977). Plans were proposed for closed incinerators to replace open-air burning of wastes (Hauze et al. 1977) and use of the sellite process to eliminate the need to burn red water. Other sources of air pollution from Volunteer AAP were reduced in the mid-1970s by installation of a new ammonia oxidation process for manufacturing 60 percent nitric acid, a new sulfuric acid regeneration process for manufacturing oleum and sellite, and a direct strong nitric process for manufacturing 98 percent nitric acid. These processes should reduce emissions to EPA-accepted levels (Hauze et al. 1977).

TABLE 8.12. PERMIT STANDARDS FOR WASTEWATER DISCHARGED FROM TWIN CITIES AAP[a]

Permit Source	Parameter (mg/L)	Level (Daily)	
		Maximum	Average
MWCC[b]	Cadmium	2.0	
	Chromium	8.0	
	Copper	6.0	
	Cyanide, Total	4.0	
	Lead	1.0	
	Mercury	0.1	
	Nickel	6.0	
	pH, max	10.0	
	pH, min	5.0	
	Zinc	8.0	
USEPA-EPS[b,c]	Cadmium	1.2	0.7
	Cyanide	5.0	2.7
	Lead	0.6	0.4
USEPA-EPS[b,d]	Cadmium	1.2	0.7
	Chromium	7.0	4.0
	Copper	4.5	2.7
	Cyanide, Total	1.9	1.0
	Lead	0.6	0.4
	Nickel	4.1	2.6
	Silver	1.2	0.7
	Total Metals	10.5	6.8
	Zinc	4.2	2.6

a. Data from Minnesota state permits as supplied by Oster (1985).

b. MWCC = Metropolitan Waste Control Commission; USEPA-EPS = U.S. Environmental Protection Agency Effluent Standards for the Electroplating Point Source Category (EPA-EPS) as defined in 40 CFR 413. The latter were effective on February 15, 1986.

c. These standards apply when flow is less than 10,000 gallons per calender day.

d. These standards apply when flow is equal to greater than 10,000 gallons per calender day.

9. WASTE MANAGEMENT: CURRENT AND PROJECTED PRACTICES IN AAPS

One of the objectives of modernization of AAPs is to improve the yield of the product, thereby cutting down the formation of by-products which often create pollution problems. One way to handle these by-products is to recycle them in accordance with the principles of RCRA (1976). The other way is to treat them before discharging the effluents so as to cause minimum impact on the environment. A summary of currently approved and funded plans was given in Section 4.

Pollutants generated in the operation of the AAPs and, briefly, waste management practices were discussed in Sections 5, 6, and 7. In this section are discussed in more detail the current practice and future plans for handling these wastes.

9.1 OPEN BURNING AND INCINERATION

Although open burning is still practiced in many AAPs, a definite trend towards incineration as the preferred method of disposal of waste munitions is discernible. It has recently been announced that new hazardous waste disposal furnaces will be developed and tested for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) by Midland-Ross Corporation, Cleveland, Ohio (Chemical and Engineering News 1984). Midland-Ross will focus on two types of furnaces--a kiln capable of destroying hazardous waste and deactivating potentially explosive materials and another kiln capable of decontaminating metal parts that have been in contact with hazardous materials. According to Maybury (1982), 80 percent of waste propellants and explosives are now incinerated. The common components of the waste explosives and propellants are listed in Table 9.1.

9.1.1 Open Burning

A 1978 report (Carpenter et al. 1978d) stated that a large variety of explosives, propellants, and related materials are open burned every month. Waste explosives open burned in 1974 and 1975 in different AAPs, arsenals, and depots amounted to 7900 and 5000 tons, respectively. Currently, the trend is towards closed incineration.

Burlington, as cited in Carpenter et al. (1978d), conducted gas sampling tests by burning 6 g of various explosives to determine emission factors and then extrapolated the results to a large-scale open burning of 3.8 tons of explosives for the purposes of estimating pollution emissions. These data are shown in Table 9.2 and 9.3. Secondary air pollutants from open burning of waste munitions are listed in Table 9.4.

TABLE 9.1. COMMON COMPONENTS OF WASTE EXPLOSIVES AND PROPELLANTS[a]

Waste Explosives	Waste Propellants
TNT	Aluminum
RDX, desensitized RDX, RCA	Acetone
HMX	Benzene
NH_4ClO_4	Carbon
NG	Cellulose
NC	Cellulose acetate
Nitroguanidine	Cupric salicylate
NH_4NO_3	Dibutylphthalate
$Ba(NO_3)_2$	Diethyl ether
Dinitrotoluene	Diethylphthalate
Diphenylamine	Dimethylphthalate
Ethyl centralite	Di-n-propyl adipate
2-Nitrodiphenylamine	Dioctylphthalate
Potassium nitrate	Ethyl alcohol
White compound	Lead-β-resorcylate
Tetryl	Lead-2-ethylhexoate
PETN	Lead salicylate
	Lead stearate
	Potassium sulfate
	Resorcinol
	Starch
	Sulfur
	Triacetin
	Wood's metal

a. Adapted from Carpenter et al. 1978d.

TABLE 9.2. ESTIMATED EMISSIONS FROM OPEN BURNING OF DIFFERENT EXPLOSIVES[a]

Pollutant (lb)	Burning 3.8 tons of			
	PX-9404	LX-09	Comp B-3	TNT
Carbon monoxide	23	4	19	213
Oxides of nitrogen	144	110	141	570
Hydrocarbons	0	0	0	4
Phosphorus pentoxide	49	0	0	0
Hydrochloric acid	87	0	0	0
Hydrofluoric acid	0	23	0	0
Soot	0	0	0	684

a. Adapted from Carpenter et al. 1978d.

TABLE 9.3. ESTIMATED EMISSIONS FROM OPEN BURNING OF DIFFERENT EXPLOSIVES[a]

Pollutant	Burning 3.8 Tons PX-9404	Burning 3.8 Tons LX-09	Burning 3.8 Tons Comp B-3	Burning 3.8 Tons TNT
Carbon monoxide (lbs)	23	4	19	213
Oxides of nitrogen (lbs)	144	110	141	570
Hydrocarbons (lbs)	0	0	0	4
Phosphorus pentoxide (lbs)	49	0	0	0
Hydrochloric acid (lbs)	87	0	0	0
Hydrofluoric acid (lbs)	0	23	0	0
Soot	0	0	0	684

[a]Adapted from Carpenter et al. 1978d.

TABLE 9.4. SECONDARY AIR POLLUTANTS THAT MAY RESULT FROM OPEN BURNING OF WASTE MUNITIONS[a,b]

Chemical	Present in (Some)	Potentially Hazardous Emission Products[c]
Aromatic dyes	Colored smoke-producing pyrotechnics	Dyes and decomposition products
Asbestos	Pyrotechnics	Asbestos
Barium	Pyrotechnics	BaO
Boron	Liquid propellants	Decomposition products, B_2O_3
Bromine	Pyrotechnics	HBr, Br_2
Chlorine	Pyrotechnics, propellants	HCl, Cl_2, $COCl_2$
Chromium	Pyrotechnics, decay elements	Cr_2O_3
Copper	Pyrotechnics, propellants	CuO
Fluorine	Propellants	HF
Lead	Propellants	PbO
Phosphorus (white)	Pyrotechnics (tracers and incendiaries) and ordnance	P_2O_5
Phosphorus (red)	Pyrotechnics	P_2O_5
Selenium	Delay elements	SeO_2
Strontium	Pyrotechnics	SrO
Sulfur	Explosives, pyrotechnics	SO_2, SO_3
Trinitrotoluene	Explosives	HCN

a. Secondary effluents are those expected to be emitted only in limited quantities.

b. Adapted from Carpenter et al. 1978d.

c. Emissions may be from airborne (vaporized, aerosolized, etc.) uncombusted materials as well as partially or completely combusted materials. Emissions listed are not inclusive.

9.1.2 Incineration

Various types of incinerators and their advantages and disadvantages have been discussed by Carpenter et al. (1978d) (see Table 9.5). The discussion in this section has been limited to incinerators of the following type: rotary kiln, fluidized bed, SITPA II, and pyrolytic. These have been selected on the basis of their potential application in the disposal of waste munitions and current interest.

TABLE 9.5. TYPES OF INCINERATORS[a]

Incinerator	Evaluating Organization
Air curtain	DuPont; Radford AAP
Closed pit	Energy Research and Development Administration - PANTEX
Batch box	Navy Ammunition Production Engineering Center (NAPEC)
Rotary demil furnace	Tooele Army Depot; NAPEC
Rotary kiln	Radford AAP
Fluidized bed	Exxon Research and Development; Picatinny Arsenal
Wet air oxidation (Zimpro Process)	Naval Ordnance Station
Molten salt (fused salt)	Naval Ordnance Systems Command Rockwell International
SITPA I	Tooele Army Depot
SITPA II	Tooele Army Depot
Vortex incinerator	Radford AAP
Vertical induced draft	Picatinny Arsenal
Multiple chamber	Joliet AAP

a. Adapted from Carpenter et al. 1978d.

9.1.2.1 Rotary Kiln Incinerator

In anticipation of stricter air pollution regulations from EPA as well as safety considerations, a four million dollar rotary kiln incinerator facility was installed at Radford AAP in 1978. Since then, propellants, nitroglycerin slums, HMX, RDX, and other energetic materials have been disposed of successfully in the rotary kiln incinerator.

Waste propellants and explosives are delivered in 30-gallon plastic tubs to the grinder building and unloaded onto the loading dock. Liquid explosives such as nitroglycerin are absorbed in sawdust or waste nitrocellulose for ease of handling before placement in the plastic tubs. The tubs are placed onto a conveyor which moves them to a dump hopper discharging the contents on a vibratory conveyor. Items too large for the opening to the grinder are shunted off. Next, the material passes through a metal detector, which activates a dumping mechanism if tramp metal is detected. Material is then fed through a chute to the grinder, which is a flying knife drum cutter. A copious quantity of water is sprayed onto the grinder cutter area to prevent ignition of

the material. The propellant slurry is then pumped at a rate of 150 gpm through a loop to one or both incinerators and back to the slurry tank in the grinder building. The feed to the incinerators usually runs at 3 to 4 gpm.

The incinerators are refractory lined cylinders (10 ft x 5 ft diameter) slightly inclined to the horizontal at an angle usually between 2 to 5° and rotating at a slow speed (1 to 5 rpm) (Forsten 1980). Both the speed of rotation and the rate of incineration of the furnace are variable so that the flow of material through the cylinder and the retention time for combustion can be controlled. The incinerator combustion temperature is maintained at 1000°F, and the flow is regulated for 2 to 4 seconds of residence. The afterburner (8 ft x 4.5 ft diameter) temperature is maintained at 1700°F with a residence of 1 to 2 seconds. The hot gases generated from the materials being incinerated are passed through a water quencher followed by a packed water scrubber. The scrubber discharge water is pumped to a concrete basin and cooled by spray aeration and recirculated to the quencher and scrubber. The gas flow through the system is controlled by an induced draft fan. All operations are remotely controlled and are monitored by a closed circuit television system on which various parameters such as grinder speed, amperage, and temperature are continuously displayed. Flow indicator probes are located in each line to ensure that the slurry is flowing. Also, flow indicators are provided at each pump gland and at the grinder. Flow stoppage automatically shuts down all pumps, opens all valves, and backflushes the lines with clean water to the slurry feed tank in the grinder building. All systems have audio and visual alarm and emergency shutdown devices.

By rotation, these furnaces offer the advantages of a gentle and continuous mixing of the propellants and explosives slurry, but capital and maintenance costs are high. These costs are due to the mechanical design requirements of both rigidity of the cylinder and close tolerances for the roller path drive as well as the high temperature seals between fixed and moving parts. Another major disadvantage is the adverse effect of the explosive slurry contacting the refractory lining at elevated temperatures and the detrimental effect on the refractory lining of cooling and reheating the chamber during shutdowns (Forsten 1980).

9.1.2.2 Fluidized Bed Incinerator

A fluidized bed incinerator evaluated at ARDC, Dover, New Jersey is a simple compact system using aluminum oxide as bed material. The propellant and explosives waste is converted into an aqueous slurry (25 percent by weight) as described in Section 9.1.2.1. The operation of the fluidized bed involves the forcing of air through the distributor plate, which can be controlled to a desired rate. At low rates, the bed remains in its original "settled" state, with the pressure drop along the bed increasing with the flow rate until it is equal to the downward force exerted by the bed material resting on the plate. The bed begins to expand at this point, which is called "incipient fluidization," allowing more gas to pass through the bed at the same pressure drop (Forsten 1980).

The bed of the incinerator is sized so that it can be fluidized with approximately 50 percent of the anticipated requirement of 120 percent of

stoichiometric air. This allows flexibility in the operation of the system in either a one- or two-stage combustion mode, [i.e., all the air is fed into the bottom of the bed or part of the air is fed into the bottom and part is fed into the upper portion of the bed (Forsten 1980)].

In addition to the incinerator, the system includes a slurry feed system, a cyclone particulate collector, and a stack gas analyzer (Figure 9.1). Initial test runs indicated that the incinerator operated effectively; however, the emission levels of 840 ppm NO_x, 650 ppm carbon monoxide, and 350 ppm hydrocarbon were well above the 200 ppm goal for each of these pollutants. This problem was solved by the addition of 6 percent (by weight) of nickel oxide to the aluminum bed causing a drastic reduction in the emissions from the incinerator: 57 pm NO_x, 40 ppm carbon monoxide, and 10 ppm hydrocarbon. These results demonstrate that the fluidized bed incinerator is a safe, efficient, and economical system for the disposal of munition wastes with minimal pollution (Forsten 1980).

9.1.2.3 Pyrolytic Incineration

Application of a two-step pyrolytic incineration technology to the disposal of propellant/explosive contaminated sludges has been reported by Schultz (1982). Schematic diagrams of the two-step pyrolytic incinerator, a conventional incinerator combining pyrolysis and combustion in one step, and the pyrotherm system (i.e., a pyrolytic system with heat recovery) are presented in Figures 9.2, 9.3, and 9.4. In the pyrotherm system the sludge is charged onto a rotating table and conveyed to the hot zone of the furnace. In the hot zone, organic materials are volatilized, and materials rich in oxygen are burned. The sludge is heated to 1000 to 1500°F and then passed into the cooler portion of the unit where the residue is removed from the hearth and fresh sludge is added. The process is continuous.

The advantages of the pyrotherm system are:

1. Sludges or wet solids can be easily processed without material handling problems.
2. After the sludge is charged onto the hearth, it is in a totally quiescent state until all of the energetic material has burned off. There are no impact or pinch points to cause premature detonations.

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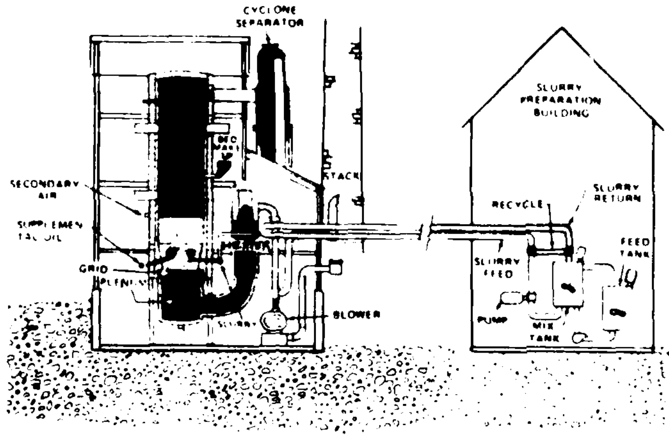

Figure 9.1. Fludized bed incinerator.
Adapted from Fosten 1980.

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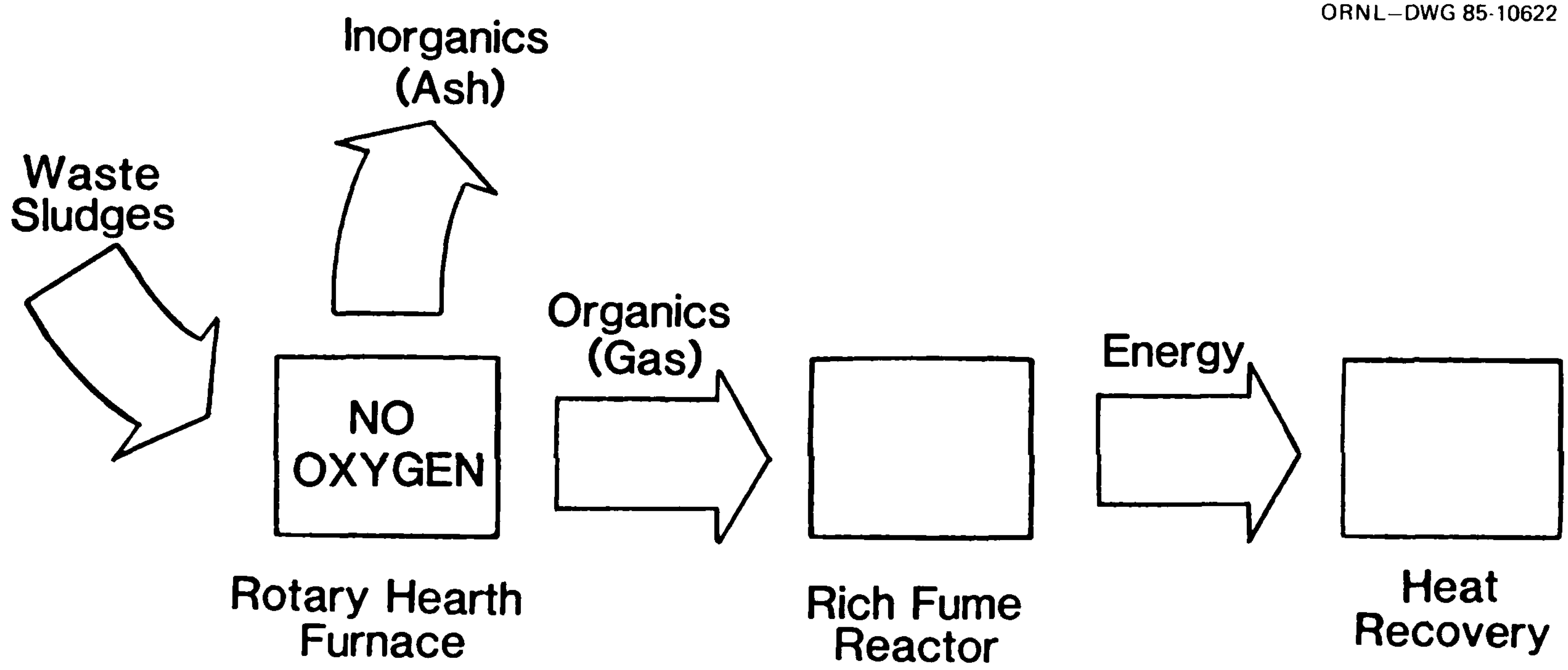

Figure 9.2. Pyrolytic incineration - two-step process. Adapted from Schultz 1982. Reprinted with permission of publisher and author.

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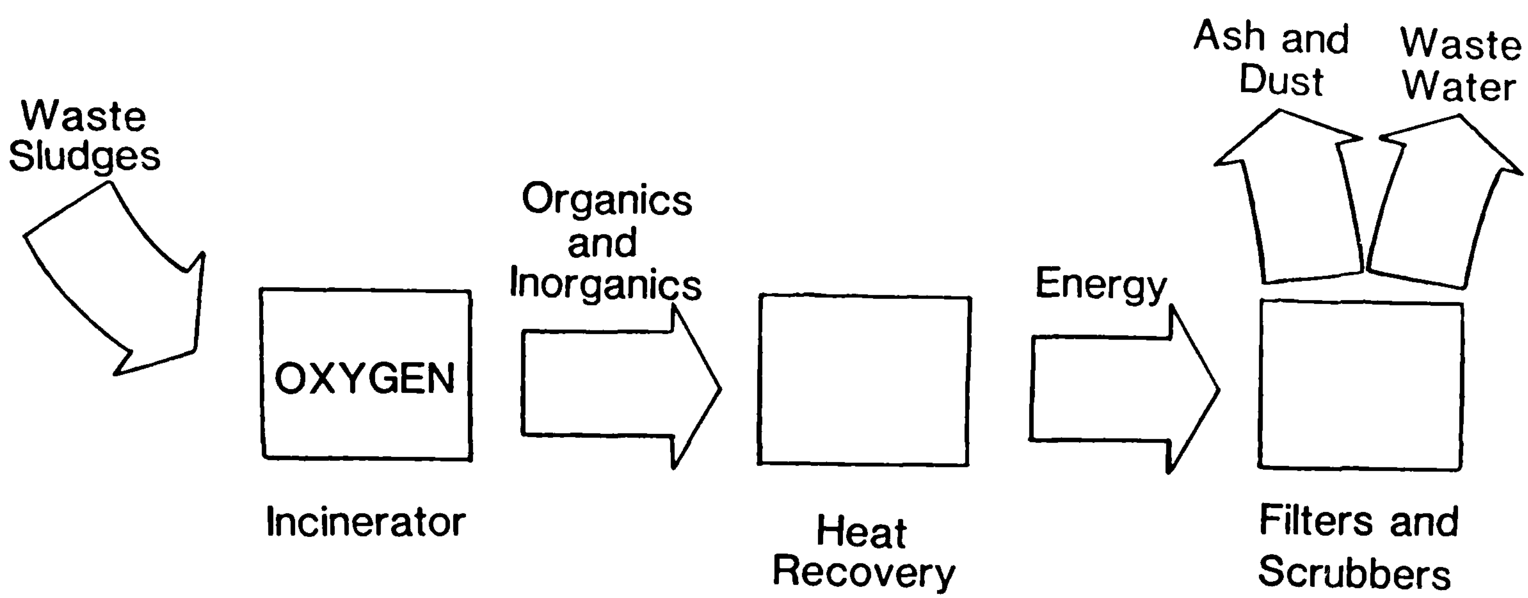

Figure 9.3. Conventional incineration - single-step process. Adapted from Schultz 1982. Reprinted with permission of publisher and author.

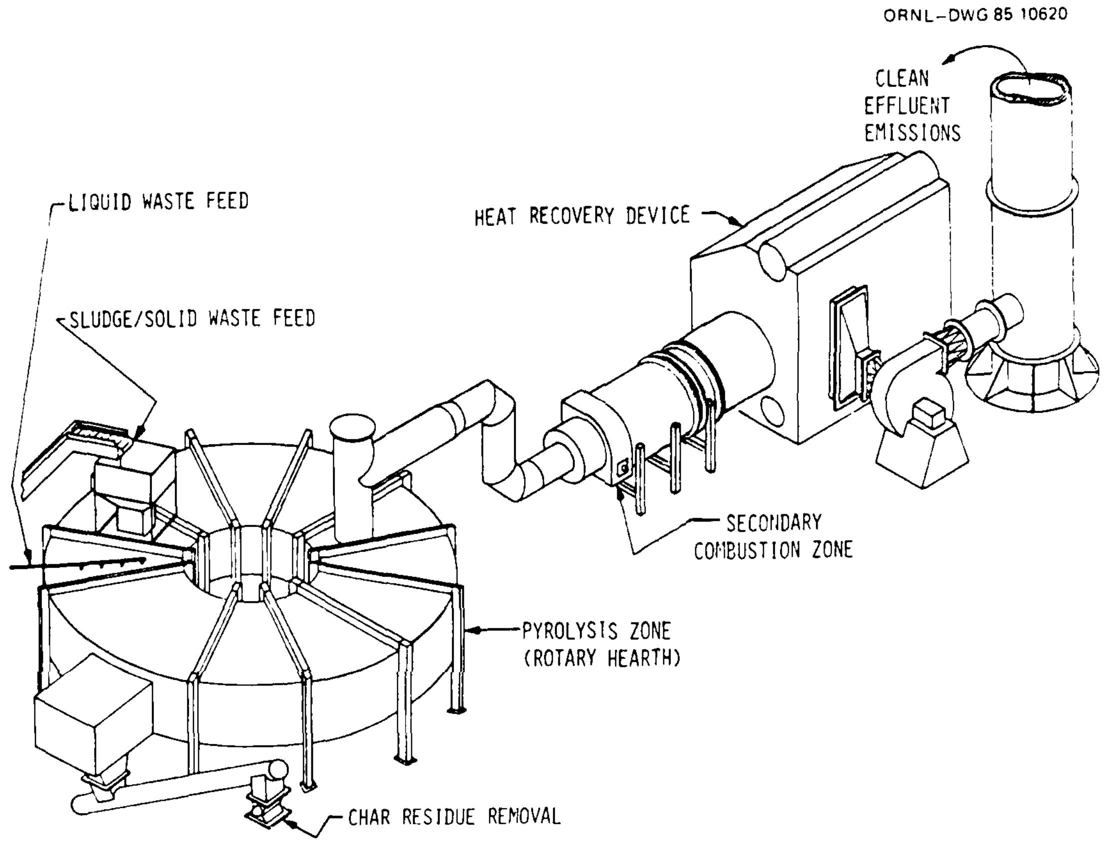

Figure 9.4. Pyrotherm system with heat recovery. Adapted from Schultz 1982.

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3. There is positive control of solids residence time and furnace atmosphere.

4. Because the residue can be rendered inert at a relatively low temperature,
the rotary hearth has a lower energy requirement than a high temperature kiln.

5. A gaseous fuel is produced that will normally result in a net production of energy.

6. The system is totally enclosed and therefore eliminates fugitive emissions from the furnace.

It is interesting to note that the PAECT program of the USATHAMA includes development of PEP (propellants, explosives, and pyrotechnics) incineration with heat recovery during the period FY 1986-88 (USATHAMA 1984).

9.1.2.4 SITPA II System

According to Forsten (1980) and Carpenter et al. (1978d), the SITPA II (Simplified Incinerator Technology for Pollution Abatement) system essentially consists of an unlined rotary kiln into which the waste propellants and explosives are dry fed into the combustion chamber in cans containing predetermined amounts of the waste and placed at intervals on a conveyor belt. The wastes are burned in the combustion chamber, which is heated by oil burners, and the combustion gases are removed from the chamber by an induction fan and passed through a cyclone particulate collector, a bag house filter, and a wet scrubber. The advantages of this system are simplicity and low capital cost. Its chief disadvantage is that, because of its dry feed system, it is more hazardous than the slurry system used in the rotary kiln and fluidized bed incinerators.

9.1.3 Conclusions

Gaps in the data on issues concerning the burning of toxic wastes have been described in a recent draft report by the Science Advisory Board of the USEPA (USEPA 1984a). While the USEPA monitors what happens to specific chemicals being burned, many new chemicals and compounds formed and released in the incineration process are not monitored or analyzed. Neither has the toxicity of the incinerator emissions to living organisms been adequately determined, nor has there been adequate study of the impact of local meteorological conditions or such events as spills and fugitive emissions of wastes. Also, there has been little documentation of adverse ecological effects or obvious health hazards from environmental exposure to incinerated toxics, and the monitoring programs used to date have been few and narrow in scope. Although it would be best if the generation of the waste could be prevented or minimized by recycling, the destruction of waste by incineration or other means is an important activity, and, in many instances, such destruction is preferable to storage in landfills or elsewhere. The Science Advisory Board emphasized a desire to

strengthen the incineration program rather than urge its discontinuation (Shabecoff 1985c). Although these remarks concerned liquid waste incineration, they apply equally well to the current practices in the AAPs.

9.2 RED WATER

Disposal of the waste sellite solution known as red water formed during the purification of TNT is a serious concern. The composition of red water is given in Table 9.6, and amounts generated at four AAPs during full mobilization are presented in Table 9.7. Red water is classified by the USEPA as a hazardous waste and must be disposed of without creating pollution in the environment. The customary disposal technique in the past has been incineration followed by landfilling of the ash. This process has been less than satisfactory for two reasons: (1) it is energy intensive and hence quite expensive, and (2) when landfilled, the ash produced a leachate with a red coloration due to the presence of unburned red water components (Helbert and Stull 1984).

TABLE 9.6. COMPOSITION OF RED WATER[a]

Component	Percentage
Water	74.6
Sodium nitrate	1.7
Sodium sulfate	0.6
Sodium sulfite	2.3
Sodium nitrite	3.5
Organics	17.3

a. Adapted from Carrazza et al. 1984.

TABLE 9.7. QUANTITY OF RED WATER AT MOBILIZATION[a]

Facility (AAP)	TNT Lines[b]	Liquid (gal/d)	Solids (lb/d)
Radford	2C	7,700	30,800
Volunteer	6C, 5B	54,200	169,400
Joliet	6C, 10B	85,200	246,400
Newport	5C	19,200	77,000

a. Adapted from Carrazza et al. 1984.

b. C = continuous line; B = batch line

During peacetime TNT is produced only at the Radford AAP. Currently, the management at Radford AAP is able to ship the red water to paper mills, where it is used to replace the sodium and sulfur lost in pulping operations. Transportation costs as well as a small processing fee are paid by the Radford facility. Although disposal by this method is advantageous, stricter pollution regulations have forced the paper mills to reduce sodium and sulfur losses, thus resulting in an uncertain market for red water (Helbert and Stull 1984). Because of this, and the potential mobilization of TNT manufacture, a closed-loop TNT purification process is being developed under the U.S. Army Manufacturing Methods and Technology (MMT) program. The Sonoco Sulfite Recovery Process (SRP), a patented process of the Sonoco Products Company, Hartsville, South Carolina, was chosen for further evaluation on the basis of level TNT production, foreign patent and scale-down problems of other methods, simplicity of design, and capital and operating costs (Carrazza et al. 1984).

The Sonoco SRP is operational in Smorgon Consolidated Industries paper mill in West Footscrae, Australia. The black liquor from wood pulping operations is converted into a solution of sodium sulfite and sodium carbonate and recycled. The proposed Radford SRP will convert TNT red water into sellite solution for reuse in the TNT purification process. The quality of the Radford SRP product is more critical than the Sonoco product because the sulfite will contact TNT and must cause no adverse chemical reaction nor leave any residual material in the TNT. A synopsis of the Radford AAP SRP is given below and a flow diagram is given in Figure 9.5.

Red water from the TNT purification, after adjustment of pH to about 6.5 to 7.0 for minimizing foaming, is concentrated to 35 percent solids in a multiple effects evaporator. It is subsequently mixed with filter cake in the repulper section of the belt filter. The resultant 36 percent solids repulper mix is pumped into a hollow shaft evaporator for further concentration to 68 percent solids. It is mixed with recycled furnace ash and petroleum coke to a solid concentration of 74 percent. This thick paste is fed into the top hearth of the multiple hearth furnace (MHF) by a screw feeder. The top six hearths of the MHF compose a reducing zone where an ash ($NaAlO_2$ + Na_2S) is formed. The ash is oxidized in the bottom two hearths of the furnace to form a mixture of $NaAlO_2$ and Na_2SO_4 (Figure 9.6). The flue gas from the MHF is composed of SO_2, CO_2, CO, H_2, H_2O, H_2S, and NO_x. It passes through an afterburner where H_2S is completely oxidized to SO_2 and H_2O and the NO_x concentration is reduced in half. The SO_2 is absorbed in the Schneible scrubber using Na_2SO_3 which is converted into $NaHSO_3$ (Figure 9.7). Any residual H_2S or SO_2 and particulate will be removed from the gas stream by another Schneible scrubber using a Na_2CO_3 solution before release into the atmosphere. The $NaHSO_3$ is treated with $NaAlO_2$ (ash from the MHF) to precipitate $Al(OH)_3$ and form Na_2SO_3 which stays in solution. The precipitated $Al(OH)_3$ is separated in a solid bowl centrifuge, and the clear Na_2SO_3 solution is recycled in TNT purification.

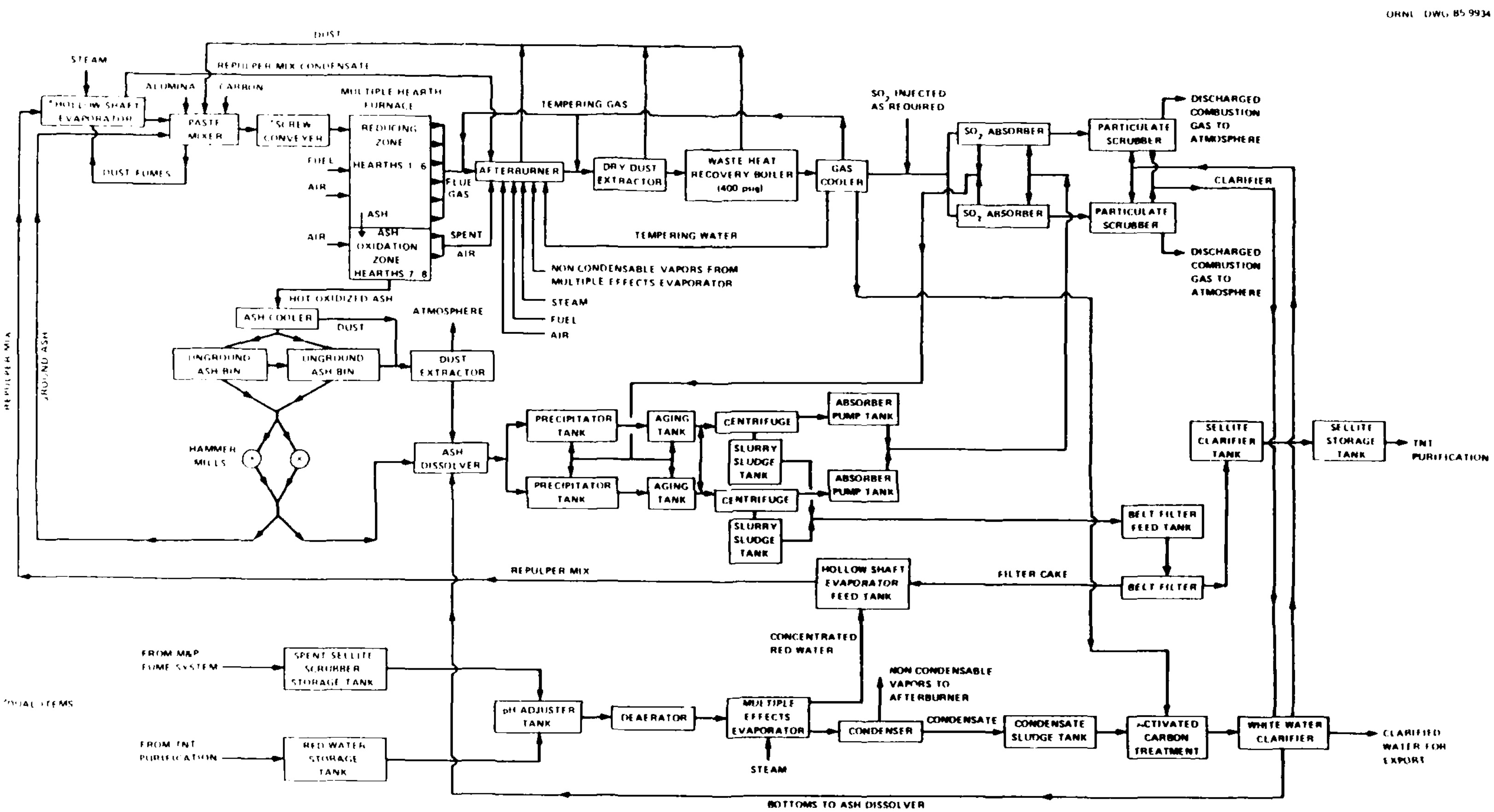

Figure 9.5. Flow diagram of Radford AAP sulfite recovery process. Adapted from Helbert and Stull 1984.

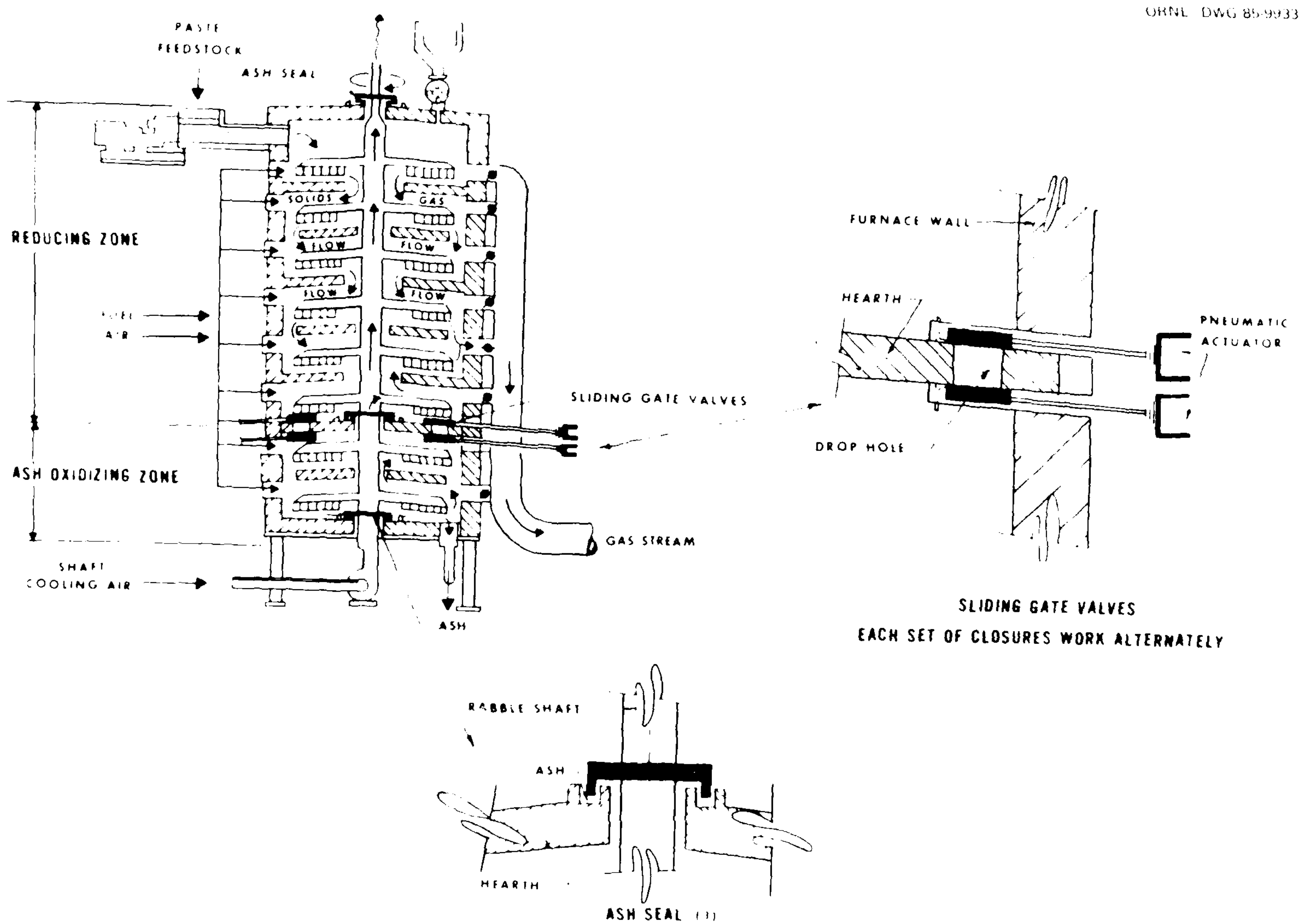

Figure 9.6. Multiple-hearth furnace, hearth seal, and sliding gate valve assembly. Adapted from Helbert and Stull 1984.

The chemical reactions taking place in the Radford AAP SRP can be summarized as follows:

(1) Na_2SO_3 (sellite) + 2 $Al(OH)_3$ (ash) + C (petroleum coke)

$$\xrightarrow{950°C, \text{ upper 6 hearths (MHF), reducing}} \underbrace{2NaAlO_2 + Na_2S}_{\text{ash}}$$

$$+ \underbrace{SO_2 + CO_2 + C + H_2O + H_2S + NO_x}_{\text{gas}}$$

(2) $Na_2S + 2O_2 \xrightarrow{820°C, \text{ lower 2 hearths (MHF)}} Na_2SO_4$ (ash)

(3) $2H_2S + 3O_2 \xrightarrow{760°C, \text{ afterburner}} 2H_2O + 2SO_2$

$2CO + O_2 \longrightarrow 2CO_2$

(4) $SO_2 + H_2O + Na_2SO_3 \xrightarrow{\text{Schneible scrubber}} 2NaHSO_3$

(5) $NaHSO_3 + NaAlO_2 + H_2O \xrightarrow{\text{Precipitator}} Na_2SO_3 + Al(OH)_3$

In summary, the Radford SRP converts red water into sellite, which is converted back into red water when used in TNT purification, a closed-loop process. The impurities from TNT are converted into water, nitrogen, and carbon dioxide, which are released to the atmosphere via the SO_2 absorber discharge stack (Figure 9.5).

Various problems arising from the adaptation of the Sonoco SRP to the Radford SRP have been investigated by a number of people (e.g., Helbert and Stull 1984; Carrazza et al. 1984).

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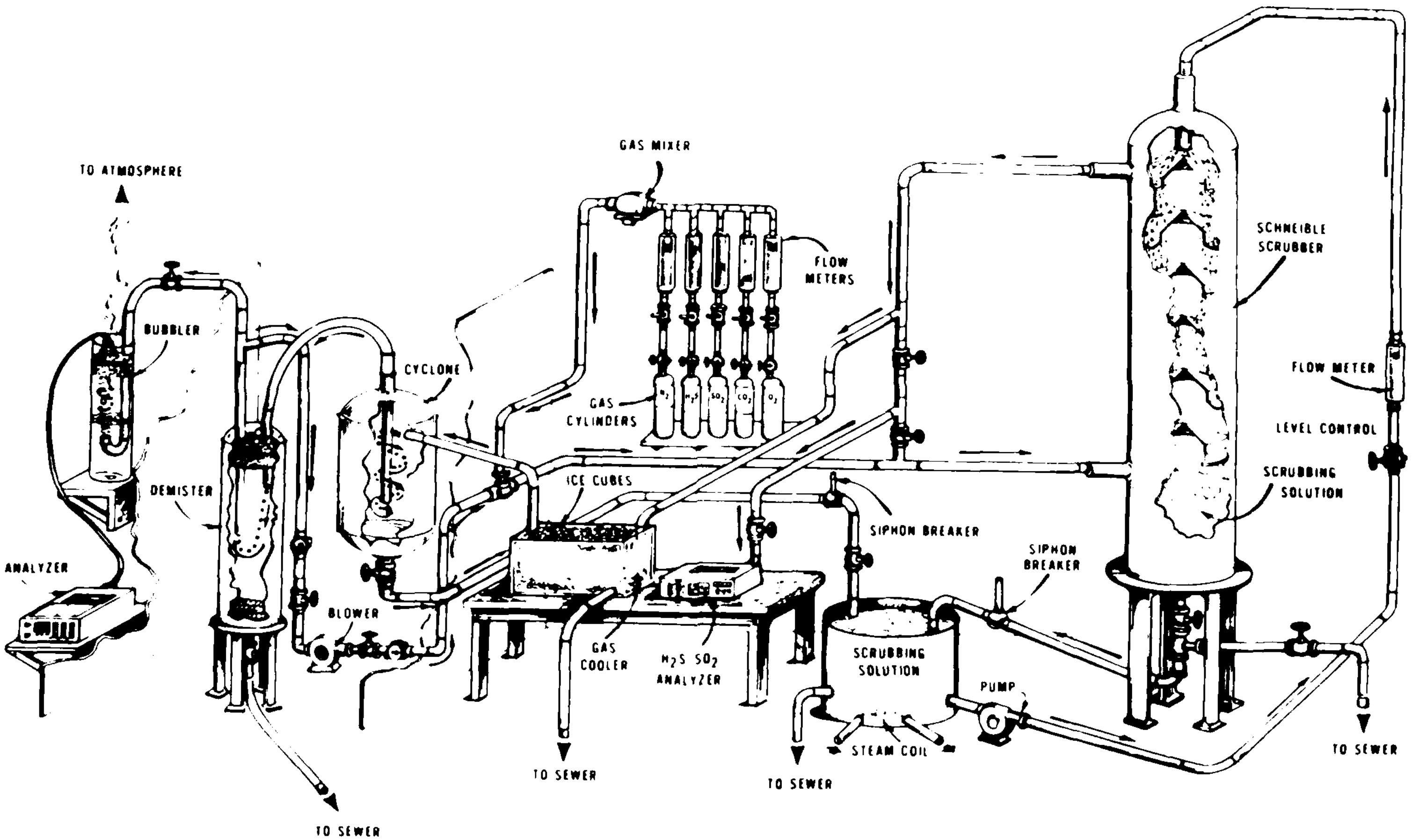

Figure 9.7. Closed circuit Schneible scrubber. Adapted from Helbert and Stull 1984.

Sodium sulfide formed during Reaction 1 (Section 9.2) has been successfully converted into innocuous sodium sulfate in the bottom two hearths of the MHF under oxidizing conditions (Reaction 2).

The solid bowl centrifuge has been used successfully to separate $Al(OH)_3$, rich with Na_2SO_3, from an aging tank slurry. The sludge, $Al(OH)_3$, is ultimately used in ash preparation, while the separated Na_2SO_3 can be used in the absorber as a scrubbing fluid or in TNT purification.

Afterburner studies have indicated that H_2S can be burnt into H_2O and SO_2 with a minimum formation of NO_x (Reaction 3, Section 9.2).

Using a 16 percent Na_2SO_3 scrubbing solution at 74°C in a six-tray Schneible scrubbing tower, complete removal of SO_2 from a synthetic afterburner gas containing 4 to 5 percent O_2 and 5000 ppm SO_2 was attained.

Additional design criteria from the results of engineering evaluations of the different components of the Radford SRP have been incorporated into FY 1985 MEA Project 60, Treatment of TNT Thick Liquor for Red Water Pollution Abatement at Radford AAP (Saffian 1985). The problem of continued accumulation of Na_2SO_4 in the recovered Na_2SO_3 needs further investigation.

9.3 PINK WATER

Pink waters are aqueous effluents that result from TNT contact with plant cleanup and scrubber water during manufacturing and Load, Assemble and Pack (LAP) operations and as a condensate from red water evaporative concentration and incineration (Patterson et al. 1976). The characteristic pink color is due to the photodegradation products of TNT. The pink constituents are a group of ill-defined water-soluble (and organic-insoluble) anions, some of which display free-radical characteristics, and they appear to constitute the major proportion of the products of TNT photolysis. Another group of photolytic TNT degradation products is extractable from water by organic solvents (Dacre and Rosenblatt 1974); most of the components of this fraction have been identified by gas chromatography, mass spectrometry, and ^1H-nuclear magnetic resonance with authentic compounds (Table 9.8). In addition to TNT, other constituents initially present in wastewaters remain after the pink color becomes manifest with the concomitant reduction in TNT. These constituents vary with the source as shown in Table 9.9. The most important, from a toxicological point of view, appear to be the DNT isomers, especially 2,4-DNT and 2,6-DNT.

The quantity and concentration of nitrobodies in pink water varies widely due to different operating conditions, although under mobilization conditions nitrobody concentrations of 140 to 160 mg/L TNT and 85 to 90 mg/L RDX at volumes of 100,000 gal per day per line are typical. (Forsten 1980).

TABLE 9.8. PHOTODEGRADATION PRODUCTS IDENTIFIED IN ORGANIC SOLVENT EXTRACTS OF PINK WATER

Photolysis Products	In Pink Water[a]	In Photolyzed TNT/RDX Mixtures[b]
1,3,5-Trinitrobenzene	x	x
2,4,6-Trinitrobenzaldehyde	x	x
2,4,6-Trinitrobenzonitrile	x	x
4,6-Dinitroanthranil	x	x
4,4'-Dimethyl-3,3',5,5'-tetranitroazoxybenzene	x	
Unidentified 3-azoxy compounds	x	
2,4,6-Trinitrobenzyl alcohol		x
Unchanged constituents, e.g., DNT-isomers	x	
3,3',5,5'-Tetranitroazoxybenzene-2,2'-dicarboxylic acid		x
3,3',5,5'-Tetranitroazobenzene-2,2'-dicarboxylic acid		x
3,3',5,5'-Tetranitroazoxybenzene-2-carboxylic acid		x

a. Data from Dacre and Rosenblatt 1974.

b. Data from Spanggord et al. 1978.

TABLE 9.9. CONSTITUENTS OF PINK WATER (OTHER THAN THOSE DERIVED FROM α-TNT) FROM VARIOUS SOURCES[a]

Source	Constituents[b]
Manufacture	
Nitrator fume scrubbers	DNTs (MNTs), (all TNT isomers), (dinitro-m-cresols[c])
Red water concentrator distillate	DNTs
Mahon fog filter effluent (Volunteer AAP only)	DNTs (MNTs), (all TNT isomers), (dinitro-m-cresols[c])
Finishing building air scrubbers and washdown[d]	(DNTs)
RDX/TNT incorporation (Holston AAP)	RDX, HMX, and products associated with their manufacture
LAP plants	RDX, HMX

a. Data from Dacre and Rosenblatt 1974.

b. Parentheses mean constituents are believed present but not positively identified.

c. Nitrocresols could arise by displacement of a nitro group on any of the isomers of alpha-TNT.

d. Alpha-TNT from this source is rather pure.

9.3.1 Current Treatment of Pink Water in the AAPs

Granulated activated carbon columns are used to effectively remove the nitrobodies from pink water. The nitrobody concentration is reduced from a saturated level of 140 mg/L to a level of less than 0.3 mg/L, which complies with current regulations (Barkley 1982, see Section 11.6). The use of carbon in a one-time only basis is expensive and also pollutive because the spent (explosive-laden) carbon is destroyed by open burning (Forsten 1980).

The feasibility of reactivation of the spent carbon has been demonstrated at the Iowa AAP. Such a capability obviates the practice of open burning spent carbon and promotes the more economical use of the carbon absorption system. Following pretreatment of the pink waste water with diatomaceous earth filters to remove the bulk of suspended solids, the aqueous effluent is pumped through the carbon columns to remove the dissolved nitrobodies. The spent carbon is discharged from the column for regeneration.

The spent carbon is dewatered initially and then fed into the calciner where it is dried at 110°C. In the next step it undergoes pyrolysis at 300°C where TNT-adsorbate is removed from its surface. Steam at 20 kg/hr and carbon dioxide at 25 L/min are fed into the calciner simultaneously to induce and maintain a reducing atmosphere. The carbon is then subjected to a reactivation temperature of about 816°C, after which it is quenched with a water spray and recovered through the discharge port. An average regeneration efficiency of 92 percent has been achieved. The process is diagramed in Figure 9.8 (Forsten 1980).

Because the regeneration efficiency is only 92 percent, it is imperative that a given lot of granular activated carbon not be recycled indefinitely. Personal communication from Dr. Gilbert of the U.S. Army Armament Research and Development Command at Dover indicates that the carbon is regenerated four times at Iowa AAP. Apparently, the adsorption efficiency of the recovered carbon decreases so much that after four cycles it is discarded by open burning.

9.3.2 Hydroperm Microfiltration System for Treatment of Pink Water

The hydroperm microfiltration system has been proposed by Sundaram et al. (1981) as an alternative for treatment of pink water. This novel method for treatment of pink water is based on cross-flow filtration with thick-walled, porous plastic tubes (hydroperm tubes). Although these tubes (with micrometer-sized pores) are primarily designed for suspended solids removal, they also can achieve significant levels of high-molecular-weight dissolved solids removal. In the case of pink water, a significant amount of color is removed because the color is due to the high-molecular-weight constituents. The effluent from the hydroperm microfiltration system can be recycled in LAP operations or discharged into natural streams after further treatment with carbon. The practicality and economics of such a system have yet to be demonstrated.

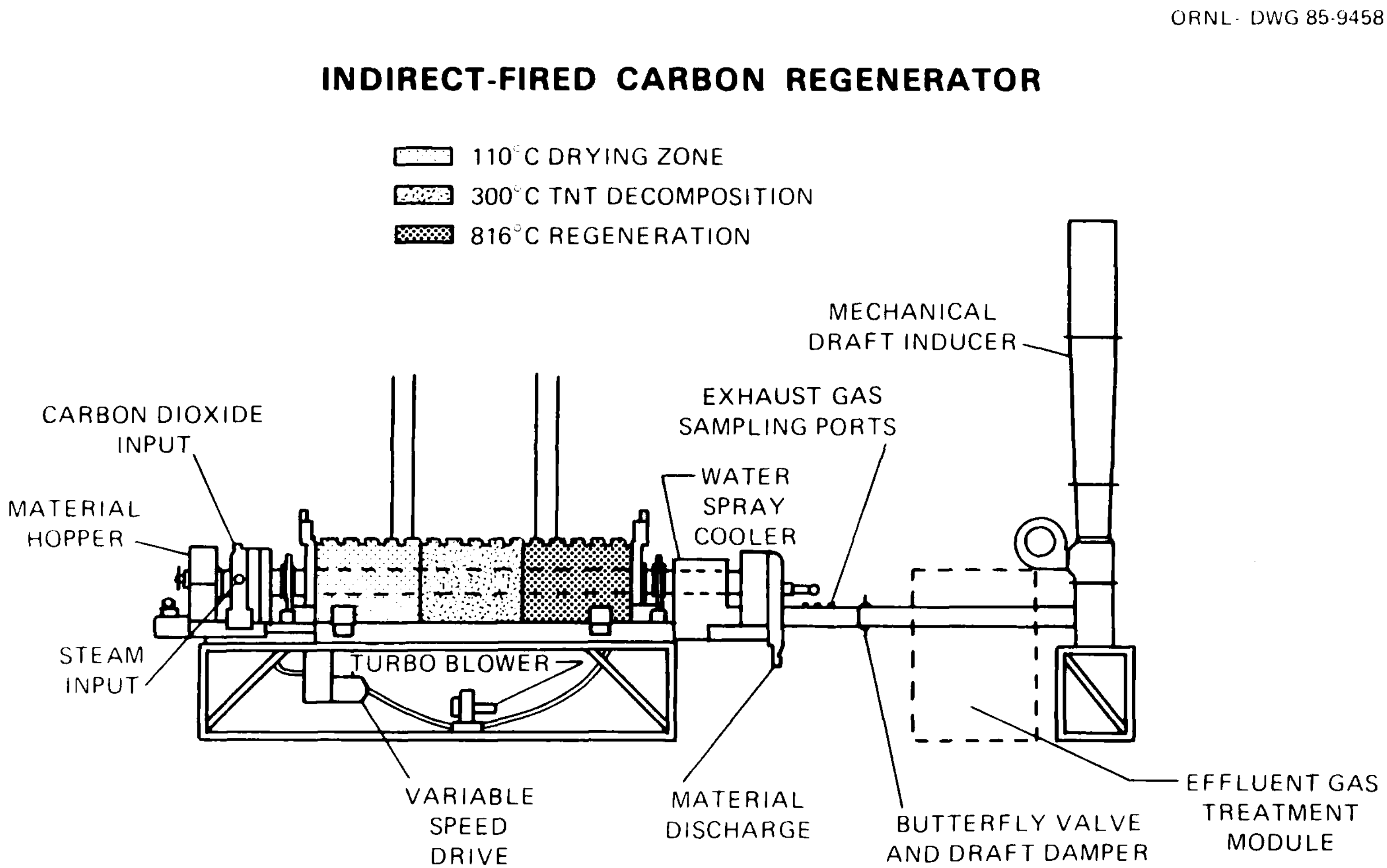

Figure 9.8. Indirect-fired carbon regenerator. Adapted from Forsten 1980.

9.3.3 Conclusions

Application of any new technology for the treatment of pink water is not planned in the current PAECT program of USATHAMA (USATHAMA 1984). However, a pilot optimization of the granular activated carbon system is under study for use in pink water treatment facilities. Several factors prompted the USATHAMA to undertake this study. Most of the existing granulated activated carbon treatment systems have been designed for low production levels and relatively high discharge limits.
Although limited performance data on removal of nitrobodies, such as DNT, and of RDX/HMX are available, additional data on removal of nitrobodies would be desirable to meet anticipated discharge standards for full capacity production to determine system modifications necessary to achieve regulatory compliance.

9.4 WASTEWATER AND SLUDGE TREATMENT

9.4.1 Wastewater Treatment

A number of laboratory-scale and pilot plant studies were carried out by Smith et al. (1983) on the treatment of wastewaters containing propellants and explosives. The objective of the laboratory-scale studies was to determine the most effective treatment method. Pilot plant studies were conducted to develop optimum design criteria.

Wastewater from nitroglycerin manufacture was found to contain dissolved nitroglycerin (NG), 1,2-dinitroglycerin (1,2-DNG), and 1,3-dinitroglycerin (1,3-DNG). Sodium sulfide was found to be effective in decomposing NG and DNG using a 30-min contact time and a wastewater at pH 10.0. Sodium sulfide requirement was found to be 2.7 lb per 1000 gallon of wastewater. Lime is also equally effective in hydrolyzing NG and DNG. NG was found to be biodegradable although it can exert a toxic or inhibiting effect on the biological metabolism. A reduction of NG concentration in wastewater from 1000 mg/L to <50 mg/L was demonstrated in a pilot plant study using lime.

Wastewater from the manufacture of other nitrate esters such as propylene glycol dinitrate, diethylene glycol dinitrate, and trimethylolethane trinitrate was investigated. These studies showed that the esters were readily decomposed by sodium sulfide, although lime or sodium hydroxide was ineffective. A pilot plant study demonstrated a reduction of the nitrate ester from 1400 mg/L to 50 mg/L in the wastewater.

Pilot plant studies indicated that a central biological treatment facility would have the capability of degrading nitroguanidine and nitrate esters in the combined manufacturing area wastewater.

However, the combined wastewater has to be pretreated to reduce the concentration of explosive materials including nitrocellulose, which is not biodegradable, to meet the Army's safety regulations.

9.4.2 Treatment and Disposal of Spent Acid Sludge from RDX/HMX Manufacture

Brundege et al. (1982) evaluated three alternatives to the current sludge treatment at Holston AAP. Treatment of the sludge with ammonia to neutralize excess nitric acid, followed by catalytic hydrogenation to destroy nitramines and residual explosives and recovery of a purified ammonium nitrate solution for resale as a fertilizer, was deemed to be most economical and attractive. Other alternatives included (1) lime neutralization of spent acid followed by calcination and recovery of lime sludge and (2) ammonia neutralization of spent acid followed by incineration of ammonium nitrate sludge.

9.4.3 Recycling of Calcium Sulfate

A bench-scale feasibility study of recycling the calcium sulfate-bearing sludge by the fluidized bed incineration method (developed by Iowa State University) has been successfully completed at Radford (Smith et al. 1983b). The quantities of wastewater sludges requiring disposal at Radford AAP at full mobilization rates are approximately 21,500 kg (23.5 tons) per day (dry weight). The SAR (sulfuric acid recovery) waste treatment plant is a major source of the calcium sulfate-containing sludge. The composition of Radford AAP sludge is: $CASO_4$ (42 percent), $Ca(OH)_2$ (2 percent), impurities (1 percent), H_2O (55 percent).

During the recycling process, dry pelletized or granulated sludge is heated in the fluidized bed reactor in alternating oxidizing and reducing atmospheres at 1200°C for 45 minutes. Natural gas is used to provide heat and create a reducing atmosphere. The conversion of $CaSO_4$ to CaO and SO_2 has been found to be 100 percent under optimum conditions. The preliminary cost analysis of the system projects a net savings of $135,795/year at Radford AAP.

9.5 BIODEGRADATION OF EXPLOSIVES AND PROPELLANTS

Biodegradation by composting has been considered as an alternative way for disposing of wastes containing explosives and propellants. However, investigations with individual explosives have revealed potential problems. These include the fact that complete mineralization may not be achieved and that the explosives and propellants may be converted into substances more toxic than the parent compounds. This is especially true for TNT. Biodegradability of selected explosive materials is discussed in the following sections.

9.5.1 Nitroguanidine and Nitrosoguanidine

According to Kaplan et al. (1982), nitroguanidine is not susceptible to aerobic biodegradation in activated sludge, and it is stable under sterile reducing conditions. However, it can be cometabolized by anaerobic sludge microorganisms to nitrosoguanidine after acclimation. There is no further microbial degradation of nitrosoguanidine. Nitrosoguanidine can decompose nonbiologically to form cyanamide, cyanoguanidine, melamine, and guanidine as shown in Figure 9.9. Both nitroguanidine and nitrosoguanidine have been found to be sensitive to ultraviolet radiation.

Recent investigations by Kaplan and Kaplan (1985a) indicate that nitroguanidine undergoes microbial degradation to ammonia in soil under continuous-flow microaerophilic conditions. The degradation product ammonia accounted for about 85 percent of the total nitrogen in nitroguanidine. Very little nitrosoguanidine was formed. Nitroguanidine can be treated on a short-term land application basis if sufficient supplemental carbon is supplied to meet the cometabolic needs.

The biodegradability of nitroglycerin and nitroguanidine has been studied by Smith et al. (1982) using a laboratory-scale rotating biological contactor. The removal of nitroguanidine was found to be dependent on the concentration of nitroglycerin. When the influent contained a COD concentration ranging from 500 to 1000 mg/L, a nitroguanidine concentration of 30 to 70 m/L, and a nitroglycerin concentration of 5 m/L, the COD removal was 90 percent, nitroguanidine removal was 50 to 90 percent, and nitroglycerin removal was 100 percent over a period of 10 days. When the nitroglycerin concentration was increased to 30 mg/L, the nitroguanidine removal greatly decreased, dropping to almost zero, 24 hours after increasing the nitroglycerin concentration.

9.5.2 N-Nitrosodimethylamine

The biodegradation of *N*-nitrosodimethylamine (NDMA) in aqueous and soil systems has been recently reported by Kaplan and Kaplan (1985b). The total percentage of NDMA mineralized increased with decreasing initial concentrations of NDMA. The rate of mineralization was reduced in aqueous systems in the presence of supplemental sources of organic matter, whereas the rate of mineralization in soil systems was unaffected by the addition of organic matter. Formaldehyde and methylamine were identified as intermediates during the biodegradation of NDMA. No hydrazine or hydrazine derivatives were detected.

9.5.3 Nitrocellulose

There is no evidence in the literature for microbial attack on nitrocellulose (Kaplan 1983a).

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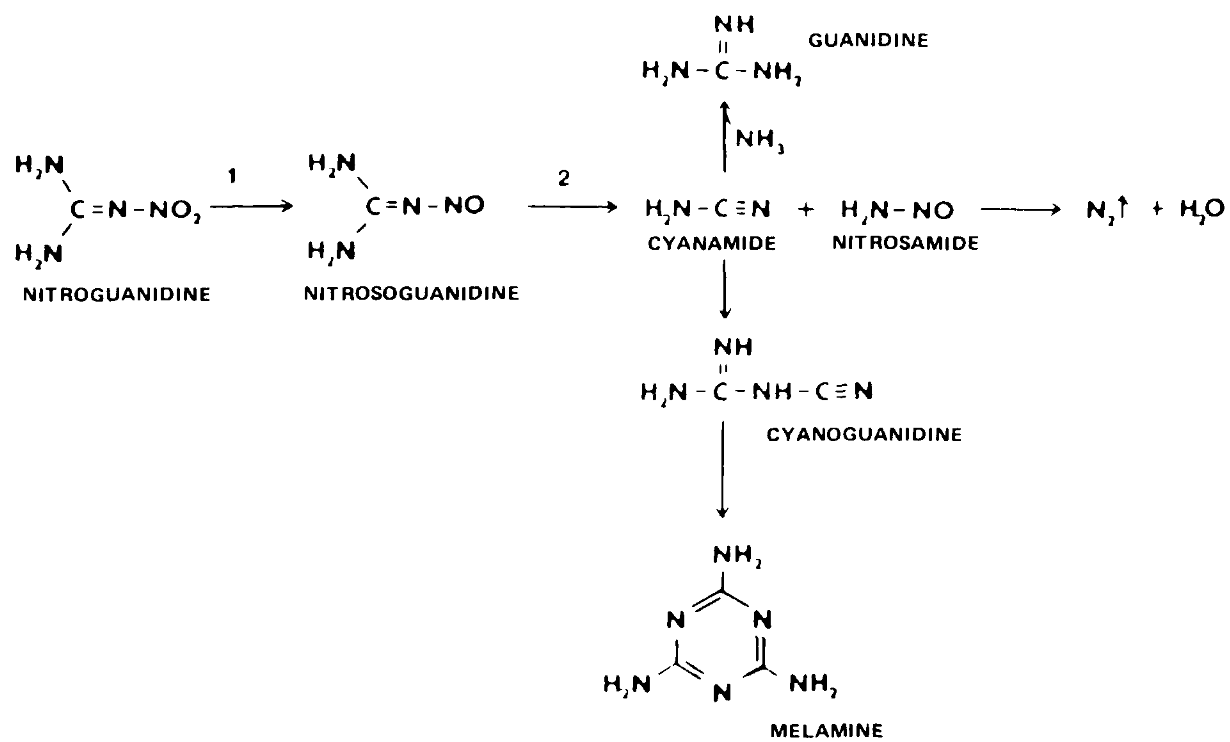

Figure 9.9. Scheme for chemical and biological degradation of nitroguanidine. Adapted from Kaplan et al. 1982.

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9.5.4 Nitroglycerin

Nitroglycerin is biodegradable, but it does exert a toxic effect on the biological metabolism of the degrading organism if sufficient readily degradable material is not present. The breakdown of nitroglycerin takes place stepwise via the dinitrate and mononitrate isomers, with each succeeding step proceeding at a slower rate (Wendt et al. 1978). After a residence time of 8 to 15 hr, none of the glycerol nitrates could be detected in the effluent from a continuous-culture apparatus supplied with an influent containing 30 mg/L of nitroglycerin.

9.5.5 Trinitrotoluene (TNT)

Microbial transformation of TNT has been studied by many investigators (Klausmeier et al. 1982; Klausmeier 1978; Kaplan and Kaplan 1982; Kaplan 1984; McCormick et al. 1976; Fowler 1965). There is general agreement that the nitro groups are reduced stepwise as a result of the action of microbes. A typical scheme is presented in Figure 9.10. In this instance, the compost consisted of horse manure, alfalfa hay, grass clippings, dead hardwood leaves, and garden soil. TNT labeled with ^{14}C was used in these experiments. A considerable amount of radioactivity was associated with the organic matter fractions from the test compost after extraction with solvents in the 24-day and 91-day composting experiments (Table 9.10). In addition, a progressively greater percentage of TNT transformation products was bound or conjugated into the organic matter fractions as the compost curing or stabilization process proceeded. Similar processes may occur with TNT in soil as well. No significant ^{14}C-labelled compounds, $^{14}CO_2$, or volatile amines were formed.

The extent of biodegradation of TNT has been debated in the literature. Kaplan (1984) concluded that TNT is not fully degraded by microbes during composting. Some earlier work (Fowler 1965) using TNT labeled with ^{14}C and bacteria from rat feces, indicated degradation of the aromatic ring of TNT to form succinic acid and amino acids. While other researchers also indicated some ring cleavage (Traxler 1975; Hale et al. 1979), breakdown of the ring structure was not found by Hoffsomer et al. (1978), Isbister et al. (1980), and Spanggord et al. (1980). Both of these groups used ^{14}C-labels to identify degradation products. Unfortunately, in the studies indicating ring cleavage, the effects of photolysis were unclear. Hale et al. mentioned this uncertainity, but no reference to it was made in the Traxler studies. Kaplan (1984) discussed shortcomings of the earlier studies indicating ring degradation and asserted that the current concensus is that the aromatic ring of TNT is not broken. Kaplan (1984) also concluded that composting is unlikely to be a viable disposal process for TNT. However, further research has been contracted to Atlantic Research Corporation to determine the effectiveness of composting TNT wastes in a pilot-plant facility (Renard 1984).

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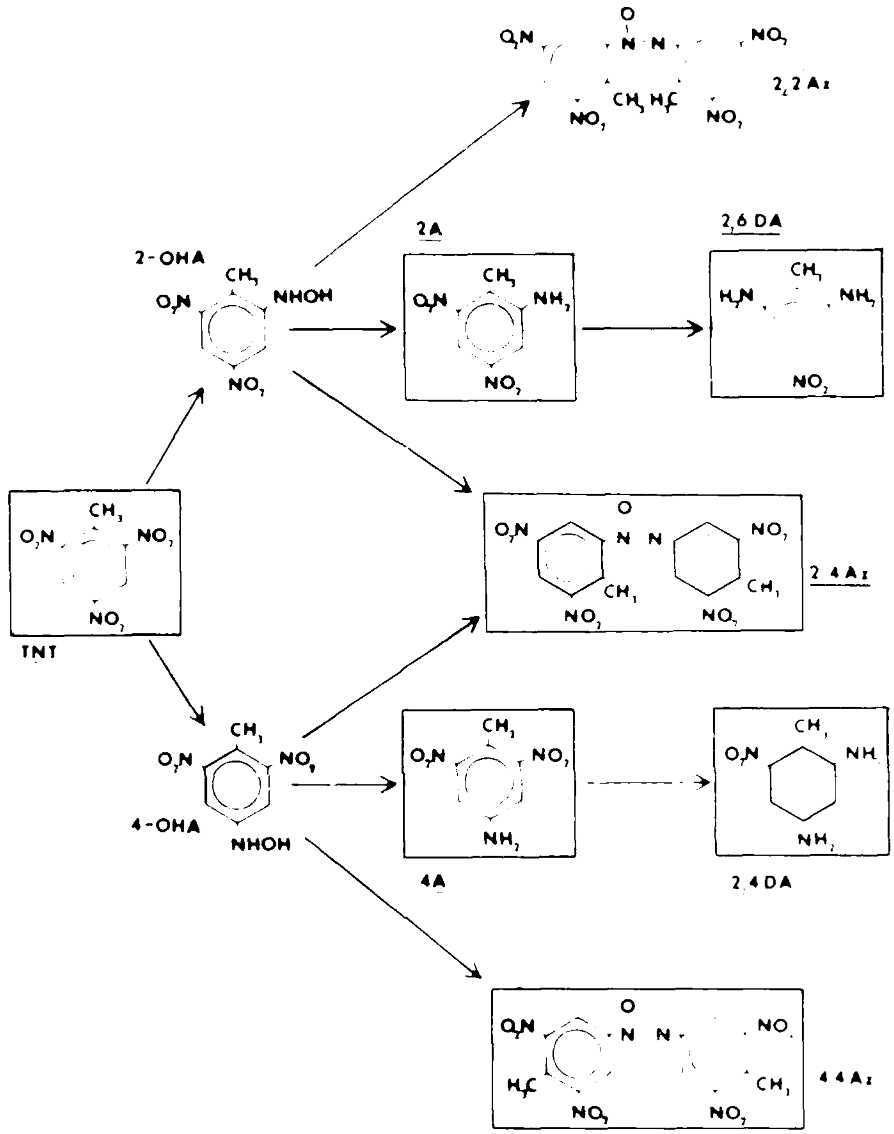

Figure 9.10. Biotransformation scheme of TNT in compost. Compounds boxed were identified in solvent extracts of the dry compost. 2-OHA, 2-hydroxyalamino-4,6-dinitrotoluene; 2,2'Az, 4,4'6,6'-tetranitro-2,2'-azoxytoluene; 2A, 2-amino 4,6-dinitrotoluene; 2,6DA, 2,6-diamino-4-nitrotoluene; 2,4'AZ, 2',4,6,6'-tetranitro-2,4'-azoxytoluene; 4-OHA, 4-hydroxylamino-2,6-dinitrotoluene; 4A, 4-amino-2,6-dinitrotoluene; 2,4DA, 2,4-diamino-6-nitrotoluene; 4,4'Az, 2,2',6,6'-tetranitro-4,4'-azoxytoluene. Adapted from Kaplan and Kaplan 1982.

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TABLE 9.10. ORGANIC MATTER FRACTIONS FROM THE TEST COMPOST[a]

Fraction	Total Radioactivity Recovered[b] (%) 24-Day Compost	91-Day Compost
Fulvic acid	0.4	0.4
Humic acid	4.0	7.8
Humin	1.3	13.9

a. Adapted from Kaplan and Kaplan 1982.

b. 3.75×10^6 dpm (initial).

9.5.6 RDX and TAX

McCormick et al. (1981) has reported that RDX is biodegraded under anaerobic conditions (anaerobic sewage sludge obtained from the Nut Island Sewage Treatment Plant, Boston, Massachusetts), yielding a number of products, including (numbers in parenthesis refer to compounds in Figure 9.11 to 9.13): hexahydro-1-nitroso-3,5,-dinitro-1,3,5-triazine (2); hexahydro-1,3-dinitroso-5-nitro-1,3,5,-triazine (3); hexahydro-1,3,5-trinitroso-1,3,5-triazine (4); hydrazine (15); 1,1-dimethylhydrazine (19); 1,2-dimethylhydrazine (23); formaldehyde (12); and methanol (17). Also shown in Figure 9.11 to 9.13 is a scheme for the biodegradation of RDX, which proceeds via successive reduction of the nitro groups to a point where destabilization and fragmentation of the ring occur. The noncyclic degradation products arise via subsequent reduction and rearrangement reactions of the fragments.

The biological treatment of RDX-containing waste must include an anaerobic mode because no reactions occur aerobically. The end products of such an operation will include hydrazines and methanol as indicated in Figure 9.12. Upon subsequent exposure to an aerobic stage, methanol will be oxidized to CO_2 and H_2O. Insufficient information is available on the biological fate of hydrazine and the dimethylhydrazines. 1,1- and 1,2-Dimethylhydrazine and their immediate precursors, dimethylnitrosamine and azoxymethane, as well as hydrazine, are recognized as mutagens, carcinogens, or both (McCormick et al. 1981).

TAX (hexahydro-1-N-acetyl-3,5-dinitro-1,3,5-triazine) is completely biodegradable in anaerobic sewage sludge cultures (McCormick et al. 1984). Two intermediates were tentatively identified as mono- and dinitroso-TAX.

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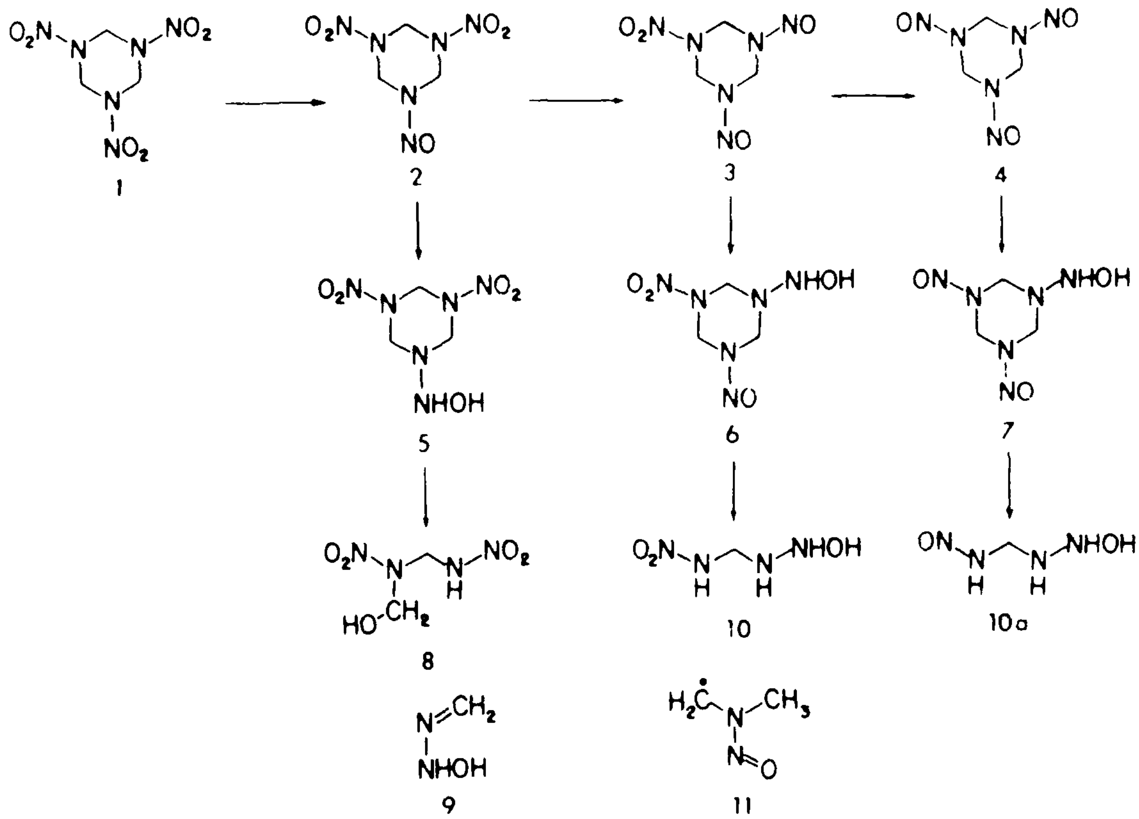

Figure 9.11. Proposed pathway for the anaerobic biodegradation of RDX compounds-I: (1) RDX; (2) MNX; (3) DNX; (4) TNX; (5) 1-hydroxylamino-3,5-dinitro-1,3,5-triazine; (6) 1-hydroxylamino-3-nitroso-5-nitro-1,3,5-triazine; (7) 1-hydroxylamino-3,5-dinitroso-1,3,5-triazine; (8) N-hydroxymethylmethylene-dinitramine; (9) N-hydroxymethylene hydrazone; (10) N-hydroxylamino-N'-nitromethylenediamine; (10a) N-hydroxylamino-N'-nitrosomethylenediamine; (11) dimethylnitrosamine radical. Adapted from McCormick et al. 1981.

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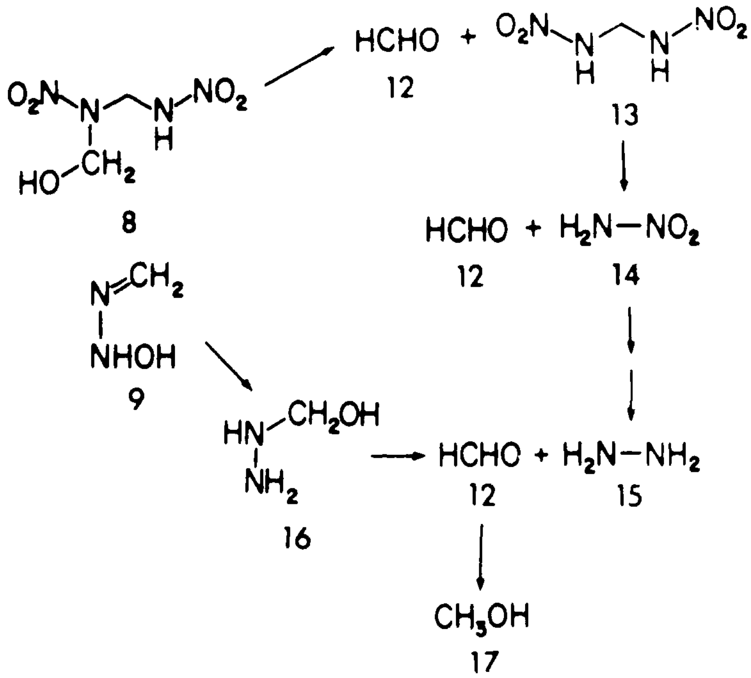

Figure 9.12. Proposed pathway for the anaerobic biodegradation of RDX compounds-II: (12) formaldehyde; (13) methylenedinitramine; (14) nitramide; (15) hydrazine; (16) hydroxymethylhydrazine; (17) methanol. Adapted from McCormick et al. 1981.

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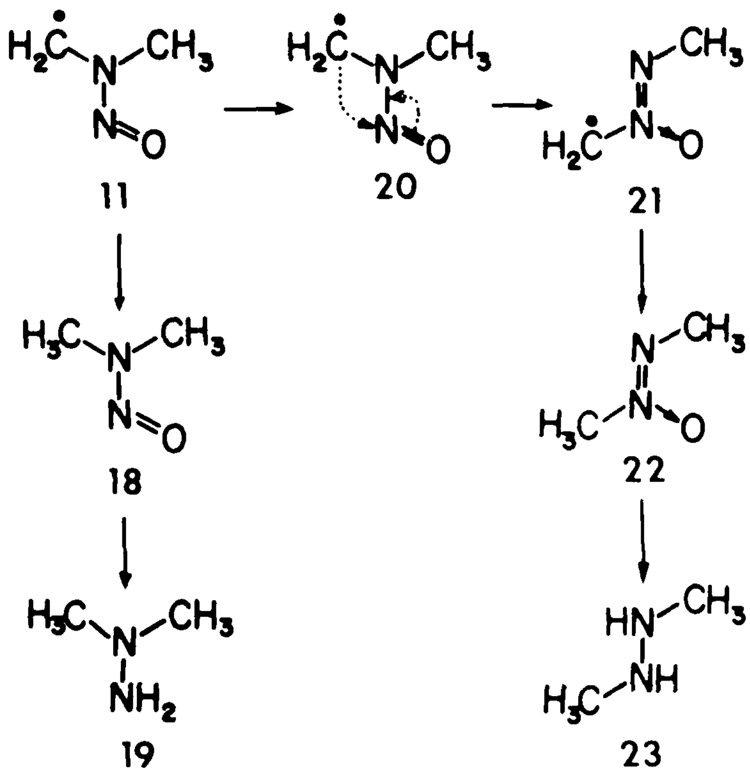

Figure 9.13. Proposed pathway for the anaerobic biodegradation of RDX compounds-III: (18) dimethylnitrosamine; (19) 1,1-dimethylhydrazine; (20) hypothetical intermediate; (21) dimethyldiazine-1-oxide, radical; (22) dimethyldiazine-1-oxide; (23) 1,2-dimethylhydazine. Adapted from McCormick et al. 1981.

9.5.7 HMX and SEX

HMX (octahydro-1-N-acetyl-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is biodegradable in anaerobic sewage sludge cultures, but complete elimination of HMX was not achieved even after several weeks of incubation (McCormick et al. 1984). Two intermediates were tentatively identified as the mono- and dinitroso- derivatives of HMX.

SEX (octahydro-1-N-acetyl-3,5,7-trinitro-1,3,5,7-tetrazocine) is biodegraded more slowly than are RDX, TAX, and HMX in anaerobic sewage sludge cultures. Two major intermediates were tentatively identified as the mono- and dinitroso- derivatives of SEX (McCormick et al. 1984).

9.5.8 Conclusions

Laboratory investigations have demonstrated the biodegradability of nitroglycerin and RDX. Nitrocellulose is not biodegradable. Although there is concensus that TNT is transformed into various aromatic compounds, the question of whether the aromatic ring of TNT is biodegradable or not needs to be resolved. Personal communication from Dave Renard of USATHAMA indicates that the Atlantic Research Corporation is currently investigating the composting of TNT.

In the Radford AAP, nitroglycerin and nitrate ester manufacturing wastewater is pretreated chemically, combined with the wastewater from propellant manufacture, and then treated biologically. The effluent thus obtained was found to be slightly more toxic to fish than the influent apparently due to the products formed during the biological treatment. More study is needed on the identification of these products (Novak 1983).

10. MONITORING POLLUTION IN AAPs

10.1 ANALYTICAL PROCEDURES

Appropriate analytical procedures for some explosives and related materials have been described in USEPA (1982b) (Table 10.1). Application of techniques such as chromatography, polarography, spectroscopy, mass spectrometry, and NMR to the analysis of explosives has been described in a recent publication by Yinon and Zitrin (1981). However, as pointed out by Novak (1983) there are some problem areas. A groundwater sampling strategy must be devised and procedures compiled for determining the reactivity of munition wastes.

Analytical methods used by Helbert and Stull (1984) for measuring emissions from the AAPs are given in Table 10.2.

10.2 BIOLOGICAL MONITORING

No information is available on the biological monitoring of workers in the AAPs. It seems reasonable to monitor workers for exposure to chemicals by analysis of blood and urine. Two examples are shown in Table 10.3.

A rather elaborate wastewater biomonitoring system was developed by Dr. David Gruber of Virginia Polytechnic Institute and State University for Radford AAP. The behavioral response of a fish exposed to irritants from the waste stream is electronically detected and amplified. This response is then compared electronically to control responses from fish exposed to normal river water. A computer statistically analyzes the signals and registers an alarm when the differences in behavior indicate that toxic levels are present (Renard 1985). This system would allow for continuous on-line monitoring of the waste stream.

TABLE 10.1. ANALYTICAL METHODS FOR SOME EXPLOSIVES AND RELATED MATERIALS CONTAINED IN SW-846[a]

Compound	Second Edition Method(s)[b] No.	Detection Limit (μg/L)
Dinitrobenzene	8090 (GC), 8250 (GC-MS)	
2,4-Dinitrotoluene	8090 (GC), 8250 (GC-MS)	5.7
2,6-Dinitrotoluene	8090 (GC)	1.9
Toluene	8020 (GC), 8024	
Antimony	7040 (AAS-DA), 7041 (AAS-FT)	
Arsenic	7060 (AAS-FT), 7061 (AAS-GH)	
Barium	7080 (AAS-DA), 7081 (AAS-FT)	
Cadmium	7130 (AAS-DA), 7131 (AAS-FT)	
Chromium	7190 (AAS-DA), 7191 (AAS-FT)	
Chromium, hexavalent	7195 (Coprecipitation), 7196 (Colormeric), 7197 (Chelation/Extraction)	
Lead	7420 (AAS-DA), 7421 (AAS-FT)	
Mercury	7470 (Manual cold-vapor technic), 7471 (Manual cold-vapor technic)	
Nickel	7520, 7521	
Selenium	7740, 7741	
Silver	7760, 7761	
Cyanides	9010	
Total organic halogen	9020	
Sulfides	9030	
Nitroaromatics and cyclic ketones	8090 (GC)	

a. Adapted from USEPA 1982b.

b. GC - Gas Chromatography; MS - Mass Spectrometry; AAS-DA - Atomic Absorption Spectroscopy - Direct Aspiration Method; AAS-FT - Atomic Absorption Spectroscopy - Furnace Technique; AAS-GH - Atomic Absorption Spectroscopy - Gaseous Hydride.

TABLE 10.2. ANALYTICAL METHODS FOR EMISSIONS FROM THE AAPs[a]

Emission	Analytical Method
NO_x	Thermo electron analyzer[b] USEPA colorimetric method[b]
CO, CO_2	Gas chromatography
O_2	Edmond oxygen analyzer and monitor
H_2S	Standard Colorimetric method
SO_2	Spectrophotometric method
$C(NO_2)_4$	Miran IR analyzer[c]
C_2H_5OH, CH_3COCH_3	Gas chromatography (Hercules 1984)
Nitroglycerin, NO_x	Samples collected in diphenylbenzidine solution by the impinger method for quantitative analysis by a colorimetric method

a. Adapted from Helbert and Stull 1984, except as noted otherwise.

b. The presence of tetranitromethane (TNM) interferes with the analysis of NO_x by this method. Measurement of NO_x on the fume recovery stack in TNT manufacture is accomplished by subtracting the interference produced by TNM (Chandler and Helbert 1980).

c. The only method found to be relatively free from interference by NO_x (Chandler and Helbert 1980).

TABLE 10.3. MONITORING OF INDUSTRIAL EXPOSURE TO CHEMICAL AGENTS[a]

Chemical Agent	Biological Parameter	Biological Material	Normal Value	Tentative Maximum Permissible Value	Remarks
Toluene	Hippuric acid	Urine	<1.5 g/g Creatinine	2.5 g/g Creatinine	
	o-Cresol	Urine	<0.3 mg/g Creatinine	1 mg/g Creatinine	
	Toluene	Blood		0.1 mg/100 mL	During exposure
	Toluene	Blood		20 ppm	During exposure
Acetone	Acetone	Urine	<2 mg/g Creatinine	20 mg/g Creatinine	
	Formic acid	Urine			
	Acetone	Blood	<0.2 mg/100 mL	2 mg/g Creatinine	
	Acetone	Expired air			

a. Adapted from Lauwreys 1983.

11. REGULATORY ASPECTS

Environmental pollution was a minor concern when the AAPs were operated under the pressures of World War II production demands. However, increased public awareness of this subject during the late 1960s eventually resulted in Executive Order 11597, dated February 1970, and later superseding orders which required all federal facilities to conform to federal environmental standards (Zeigler 1980).

11.1 EMISSION FACTORS

Emission factors which can be used for calculating emissions from AAPs have been published by the USEPA. The limited applicability of these factors has been emphasized by the Agency. The following excerpt is from USEPA (1980a).

"The limited applicability of emission factors must be understood. To give some notion of the accuracy of the factors for a specific process each set of factors has been ranked according to the amount of data upon which it is based. In the past, Sections [(i.e., a group of pollutants, see Table 11.2)] have been rated only as a whole. Future updates, to the degree possible, will include ratings by pollutant for each process. Each rating has been based on the weighing of various information categories used to obtain the factor(s). These categories and associated numerical values are:

"Measured emission data: 20 points maximum
"Process data: 10 points maximum
"Engineering analysis: 10 points maximum

"The emission data category rates the amount of measured source test data available for the development of the factor(s). The process data category involves such considerations as variability of the process and resultant effect on emissions, as well as the amount of data available on these variables. Finally, the engineering analysis category is concerned with data upon which a material balance or related calculation can be made. Depending on which information categories are employed to develop it, each set of factors is assigned a numerical score of from 5 to 40 points. Each numerical score, is, in turn, converted to letter ratings which are presented throughout this publication [(<u>Compilation of Air Pollutant Emission Factors</u>, USEPA)] as follows:

"Numerical Rating	Letter Rating
5 or less	E (Poor)
6 to 15	D (Below average)
16 to 25	C (Average)
26 to 35	B (Above average)
36 to 40	A (Excellent) "

The emission factors for sulfuric acid plants are given in Table 11.1. Table 11.2 lists the emission factors in the manufacture of TNT and nitrocellulose. The footnote "a" mentions the emission of toluene and trinitromethane. The latter may be a citation error. It should probably read tetranitromethane. Emission factors for the open burning of TNT were determined by the USEPA (1983a) using very small amounts of TNT in a simulated open burn experiment. Thus the following factors (given in lb pollutant per ton TNT burned) should be used with caution: particulates (soot) 180.0, nitrogen oxides 150.0, carbon monoxide 56.0, and volatile organic compounds (non-methane) 1.1.

TABLE 11.1. EMISSION FACTORS (RATING A) FOR SULFURIC ACID PLANTS[a]

Conversion of SO_2 to SO_3 (%)	SO_2 Emissions kg/Mg of 100% H_2SO_4	SO_2 Emissions lb/ton of 100% H_2SO_4
93	48.0	96
94	41.0	82
95	35.0	70
96	27.5	55
97	20.0	40
98	13.0	26
99	7.0	14
99.5	3.5	7
99.7	2.0	4
100	0.0	0

a. Adapted from USEPA 1981a.

The acid mist emission factors for sulfuric acid plants without controls are listed in Table 11.3. Comparative efficiency of electrostatic precipitators vs. fiber mist eliminators is presented in Table 11.4. The emission factors for nitrogen oxide from nitric acid plants are listed in Table 11.5.

The source classification codes and the corresponding emission factors are listed in Table 11.6 for TNT and nitrocellulose production.

TABLE 11.2 EMISSION FACTORS (RATING C) FOR EXPLOSIVE MANUFACTURING[a,b]

Process	Particulates kg/Mg	Particulates lb/ton	Sulfur Dioxides kg/Mg	Sulfur Dioxides lb/ton	Nitrogen Dioxides kg/Mg	Nitrogen Dioxides lb/ton	Nitric Acid Mist kg/Mg	Nitric Acid Mist lb/ton	Sulfuric Acid Mist kg/ton	Sulfuric Acid Mist lb/ton
TNT - Batch Process[c]										
Nitration reactors										
Fume recovery	-	-	-	-	12.5 (3-19)	25 (6-38)	0.5 (0.15-0.95)	1 (0.3-1.9)	-	-
Acid recovery	-	-	-	-	27.5 (0.5-68)	55 (1-136)	46 (0.005-137)	92 (0.02-275)	-	-
Nitric acid concentrators	-	-	-	-	18.5 (8-36)	37 (16-72)	-	-	4.5 (0.15-13.5)	9 (0.3-27)
Sulfuric acid concentrators[d]										
Electrostatic precipitator (exit)	-	-	7 (2-20)	14 (4-40)	20 (1-40)	40 (2-80)	-	-	32.5 (0.5-94)	65 (1-188)
Electrostatic precipitator with scrubber[e]	-	-	Trace	Trace	20 (1-40)	40 (2-80)	-	-	2.5 (2-3)	5 (4-6)
Red water incinerator										
Uncontrolled[f]	12.5 (0.015-63)	25 (0.03-126)	1 (0.025-1.75)	2 (0.05-3.5)	13 (0.75-50)	26 (1.5-101)	-	-	-	-
Wet scrubber[g]	0.5	1	1 (0.025-1.75)	2 (0.05-3.5)	2.5	5	-	-	-	-
Sellite exhaust	-	-	29.5 (0.005-88)	59 (0.01-177)	-		-	-	3 (0.3-8)	6 (0.6-16)
TNT - Continuous Process[c]										
Nitration reactors										
Fume recovery	-	-	-	-	4 (3.35-5)	8 (6.7-10)	0.5 (0.15-0.95)	1 (0.3-1.9)	-	-
Acid recovery	-	-	-	-	1.5 (0.5-2.25)	3 (1-4.5)	0.01 (0.005-0.015)	0.02 (0.01-0.03)	-	-
Red water incinerator	0.13 (0.015-0.25)	0.25 (0.03-0.5)	0.12 (0.025-0.22)	0.24 (0.05-0.43)	3.5 (3-4.2)	7 (6.1-8.4)	-	-	-	-
Nitrocellulose[c]										
Nitration reactors[h]	-	-	0.7 (0.4-1)	1.4 (0.8-2)	7 (1.85-17)	14 (3.7-34)	9.5 (0.25-18)	19 (0.5-36)	-	
Nitric acid concentrator	-	-	-	-	7 (5-9)	14 (10-18)	-		-	
Sulfuric acid concentrator	-	-	34 (0.2-67)	68 (0.4-135)	-		-	-	0.3	0.6
Boiling tubs	-	-	-	-	1	2	-		-	-

a. For some processes, considerable variations in emissions have been reported. Average of reported values is shown first; ranges are in parentheses. Where only one number is given, only one source test was available. Emission factors are expressed as kilograms of pollutant per megagram and as pounds of pollutant per ton of TNT or nitrocellulose produced. Significant emissions of volatile organic compounds (VOC) have not been reported for the explosives industry. However, negligible emissions of toluene and trinitromethane from nitration reactors have been reported in TNT manufacture. Also, fugitive VOC emissions may result from various solvent recovery operations. See Section 11.1.

b. Adapted from USEPA 1983a.

c. <u>Air Pollution Engineering Source Sampling Surveys</u>. Volunteer AAP, Joliet AAP, and Radford AAP, U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, MD, July 1967, July 1968.

d. Acid mist emissions influenced by nitrobody levels and type of furnace fuel.

e. No data available for NO_x emissions after scrubber. NO_x emissions are assumed unaffected by scrubber.

f. Use low end of range for modern efficient units, high end for less efficient units.

g. Apparent reductions in NO_x and particulate after control may not be significant, because these values are based on only one test result.

h. For product with low nitrogen content (12%), use high end of range. For products with higher nitrogen content, use lower end of range.

TABLE 11.3. ACID MIST EMISSION FACTORS (RATING B) FOR SULFURIC ACID PLANTS WITHOUT CONTROLS[a]

Raw Material	Oleum Produced (% Total Output)	Emissions[b] kg/Mg acid	lb/ton acid
Recovered sulfur	0 to 43	0.175 - 0.04	0.35 - 0.8
Bright virgin sulfur	0	0.85	1.7
Dark virgin sulfur	33 to 100	0.16 - 3.15	0.32 - 6.3
Sulfide ores	0 to 25	0.6 - 3.7	1.2 - 7.4
Spent acid	0 to 77	1.1 - 1.2	2.2 - 2.4

a. Adapted from USEPA 1981a.

b. Emissions are proportional to the percentage of oleum in the total product. Use low end of ranges for low oleum percentage and high end of ranges for high oleum percentage.

TABLE 11.4. EMISSION COMPARISON AND COLLECTION EFFICIENCY OF TYPICAL ELECTROSTATIC PRECIPITATORS AND FIBER MIST ELIMINATORS[a,b]

	Particle Size Collection Efficiency (%)		Acid Mist Emissions			
			98% Acid Plants		Oleum Plants	
Control Device	>3μm	≤3μm	kg/Mg	lb/ton	kg/Mg	lb/ton
Electrostatic precipitator	99	100	0.05	0.10	0.06	0.12
Fiber mist eliminator						
Tabular	100	95-99	0.01	0.02	0.01	0.02
Panel	100	90-98	0.05	0.10	0.05	0.10
Dual pad	100	93-99	0.055	0.11	0.055	0.11

a. Adapted from USEPA 1981a.

b. Based on manufacturers' generally expected results. Calculated at 8% SO_2 concentration in gas converter.

TABLE 11.5 NITROGEN OXIDE EMISSION FACTORS (RATING B) FROM NITRIC ACID PLANTS[a,b]

Source	Control Efficiency (%)	Emissions lb/ton Acid	Emissions kg/MT Acid
Weak acid plant tail gas			
Uncontrolled[c]	0	43 (14-86)	22 (7-43)
Catalytic reduction			
Natural gas[c]	99.1	0.4 (0.05 - 1.2)	0.2 (0.03 - 0.6)
Hydrogen[d]	97 - 99.8	0.8 (0 - 1.5)	0.4 (0 - 0.8)
Natural gas/hydrogen (25%/75%)[e]	98 - 98.5	1.0 (0.8 - 1.1)	0.5 (0.4 - 0.6)
Extended adsorption[c]	95.8	1.8 (0.8 - 2.7)	0.9 (0.4 - 1.4)
High strength acid plant[f]	NA[g]	10	5

a. Based on 10% acid. Production rates are in terms of total weight of product (water and acid). A plant producing 500 tons (454 metric tons (MT))/day of 55 wt. % nitric acid is calculated as producing 275 tons (250 MT)/day of 100% acid. Ranges in parentheses.

b. Adapted from USEPA 1980b.

c. Based on a study of 18 plants.

d. Based on data from two plants with these process conditions: production rate, 130 tons (118 MT)/day at 100% rated capacity; absorber exit temperature, 90°F (32°C); absorber exit pressure, 87 psig (600 kPa); acid strength, 57%.

e. Based on data from two plants with these process conditions: production rate, 208 tons (188 MT)/day at 100% rated capacity; absorber exit temperature, 90°F (32°C); absorber exit pressure, 80 psig (550 kPa); acid strength, 57%.

f. Based on a unit that produces 3000 lb/hr (6615 kg/hr) at 10% rated capacity, of 98% nitric acid.

g. NA - Not Available

TABLE 11.6 NATIONAL EMISSION DATA SYSTEM SOURCE CLASSIFICATION CODES AND EMISSION FACTORS LISTING[a]

Source Classification Code	Process	Emissions (lb)/Production (Ton)		
		Particulates	SO_x	NO_x
<u>Major Group 28</u>[b]				
<u>Group 289</u>				
<u>TNT - 2892</u>				
3-01-010-11	Batch process - nitration reactors fume recovery			25.0
3-01-010-12	Batch process - nitration Reactors acid recovery			55.0
3-01-010-13	Batch process - nitric acid concentrators			37.0
3-01-010-14	Batch process - sulfuric acid concentrators - electrostatic precipitators (exit)		14.0	40.0
3-01-010-15	Batch process - red water incinerator	25.0	2.00	26.0
3-01-010-21	Continuous process - nitration reactors (fume recovery)			8.00
3-01-010-22	Continuous process - nitration reactors (acid recovery)			3.00
3-01-010-23	Continuous process - red water incinerator	0.25	0.24	7.00
<u>NC - 2892</u>				
3-01-041-01	Nitration reactors	0.00	1.40	14.0
3-01-041-02	Sulfuric acid concentrator	0.00	68.0	0.00
3-01-041-03	Boiling tubs	0.00	0.00	2.00
3-01-041-04	Nitric acid concentrator	0.00	0.00	14.0

a. Adapted from USEPA (1979b).

b. Major group 28 is chemical and allied products; group 289 is miscellaneous chemical products; and 2892 contains both nitrocellulose (NC) and TNT.

11.2 PERFORMANCE STANDARDS

11.2.1 EPA Performance Standard for New and Modified Plants

It is evident from Tables 11.3, 11.4, and 11.5 that when best available technology is used, the USEPA performance standards for new and modified sulfuric and nitric acid plants can usually be satisfied.

Sulfuric acid plants- SO_2 emission, 2 kg/Mg (4 lb/ton) of 100 percent sulfuric acid, maximum 2-hour average (USEPA 1981a). This emission standard is met when the conversion of SO_2 to SO_3 is 99.7 percent (see Table 11.1). Sulfuric acid mist emission, 0.075 kg/Mg (0.15 lb/ton) of 100 percent acid (USEPA 1981a). [Electrostatic precipitators and fiber mist eliminators, if properly maintained, can effectively meet this requirement (see Table 11.4)].

Nitric acid plants- Nitrogen oxide emissions [(expressed as NO_2, 3.0 lb/ton (15 kg/MT)] of 100 percent acid produced, maximum, 3-hour average (USEPA 1980b). High strength acid plants emit 10 lb (NO_x) per ton of acid produced (see Table 11.5).

11.2.2 Virginia Air Pollution Standards for Sulfuric Acid and Nitric Acid Manufacture

The AAPs located in Virginia (e.g., Radford AAP) are affected by the following State Air Pollution Standards (VAPCR 1983) for sulfur dioxide and nitrogen oxides emissions:

> "The sulfur dioxide in the tail gases from any sulfuric acid manufacturing operation shall not exceed a concentration of 2000 parts per million by volume and a mass emission rate of 27 lbs/ton of 100 percent acid produced when elemental sulfur is used for feed material, or 3500 ppm by volume and a mass emission rate of 45 lbs/ton of 100 percent acid produced when other raw materials such as recycled spent acid and ores are used as feed. These emission levels may be exceeded for a period not longer than 24 hours during start-up.
>
> "Nitric Acid Manufacture -- No owner or other person shall cause, suffer, allow or permit the emission of nitrogen oxides (expressed as nitrogen dioxide) from nitric acid manufacturing plants into the outdoor atmosphere in excess of 5.5 pounds per ton of 100 percent acid produced."

11.3 EPA REGULATIONS FOR EXPLOSIVES AND RELATED MATERIALS

The waste propellant, explosive, and pyrotechnic (PEP) materials are listed under the EPA hazardous waste numbers K044, K045, K046, and K047 and classified as reactive and toxic hazardous wastes (Table 11.7). Solvents used in the processing of explosives have also been classified as a hazardous waste (Table 11.7).

TABLE 11.7. HAZARDOUS WASTES FROM SPECIFIC AND NONSPECIFIC SOURCES[a]

Industry and USEPA Hazardous Waste No.	Hazardous Waste	Hazard Code[b]
<u>Explosives:</u>		
K044	Wastewater treatment sludges from the manufacture and processing of explosives	R
K045	Spent carbon from the treatment of wastewater containing explosives	R
K046	Wastewater treatment sludges from the manufacturing, formulation, and loading of lead-based initiating compounds	T
K047	Pink/red water from TNT operations	R
<u>Generic:</u>		
F003	The following spent nonhalogenated solvents- xylene, acetone, ethyl acetate, ethylbenzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol- and the still bottoms from the recovery of these solvents	I

a. Adapted from USEPA 1983b and USEPA 1983c.

b. R = reactive waste; T = toxic waste; I = ignitable waste.

Considerable emphasis has been placed on the development of PEP incineration systems capable of meeting not only state and local air pollution statutes, but also stringent RCRA hazardous waste incinerator performance standards (USEPA 1981b). These standards include 99.99 percent destruction and removal of designated principal organic hazardous constituents, a 99 percent HCl removal efficiency for chlorine containing (0.5 percent or greater) waste streams, and a particulate grain loading standard of 0.08 gr per dry standard cubic feet corrected to 50 percent excess air in the stack gas or for the amount of oxygen in the stack gas according to the formula, $P_c = P_m \, 14/(21 - Y)$, where P_c is the corrected particulate concentration, P_m is the measured particulate concentration, and Y is the oxygen concentration in the stack gas (Orsat-method) (USEPA 1983e). The standards serve as a basis for the EPA to write site-specific RCRA permits for hazardous waste incinerators. Typically, such Part B permit applications should contain: (1) general information (waste analysis, security procedures, inspection schedules, contingency plans, etc.); (2) trial burn results, and (3) operational data (waste/air feed rates, combustion temperature, residence time, stack gas flow rate/temperature) (Wood 1982).

The USEPA incineration regulations (USEPA 1981b) provide a mechanism for exemption from compliance with performance standards for those incinerators which burn only ignitable hazardous material. Recent revision (USEPA 1982a) has extended the exemption to include corrosive and some reactive hazardous wastes provided that such PEP materials will not be burnt when other hazardous wastes are present in the combustion zone and that the waste analysis reveals no hazardous constituents as listed in Appendix VIII, 40 CFR 261. The revised regulations also provide for exemption (at the discretion of the Regional USEPA) of incinerators burning insignificant amounts (typically less than 100 ppm) of designated hazardous constituents (Wood 1982).

11.4 OPEN BURNING OF WASTE EXPLOSIVES

As stated in USEPA (1984d),

> "Open burning of hazardous waste is prohibited except for the open burning and detonation of waste explosives. Waste explosives include waste which has the potential to detonate and bulk military propellants which cannot safely be disposed of through other modes of treatment. Detonation is an explosion in which chemical transformation passes through the material faster than the speed of sound (0.33 kilometers/second at sea level). Owners or operators choosing to open burn or detonate waste explosives must do so in accordance with the following table (see Table 11.8) and in a manner that does not threaten human health or the environment."

TABLE 11.8. SITE LOCATION FOR OPEN BURNING OR DETONATION OF WASTE EXPLOSIVES[a]

Pounds of Waste Explosives or Propellants	Minimum Distance from Open Burning or Detonation to the Property of Others
0 to 100	204 meters (670 feet)
101 to 1,000	380 meters (1,250 feet)
1,001 to 10,000	530 meters (1,730 feet)
10,001 to 30,000	690 meters (2,260 feet)

a. Adapted from USEPA 1984d.

According to Sandrin (1982), there are currently no standard tests available to evaluate the reactivity of waste residue and soil samples. Such tests are needed to verify the actual effectiveness of open burning/open detonation in destroying the waste explosives. Also, there are currently no environmental standards for acceptable soil and water concentrations of munition compounds nor are there any readily available data to evaluate the mobility of these compounds in the environment.

11.5 TOXIC WASTE DUMPS ON MILITARY BASES

Shabecoff (1985b) has reported that the USEPA has proposed a major overhaul of its guidelines for the cleanup of toxic waste dumps in an effort to speed up the process and define how clean the sites must be. The proposed changes will allow waste sites on federal facilities, such as military bases, to be included in the priority list. However, the five-year, $1.6 billion fund set up under the Comprehensive Environmental Response Compensation and Liability Act of 1980 cannot cover the expense of cleaning up the toxic waste dumps on military bases, and, moreover, the military sites are not eligible under the law to receive money from the fund, which is now built largely from an excise tax on chemicals. The cost of cleaning up 500 to 800 bases, weapons production facilities, missile installations, and other military facilities has been estimated to be $5 to 10 billion according to Carl Schafer, Director for Environmental Policy, Department of Defense (Shabecoff 1985d).

11.6 RECOMMENDED INTERIM ENVIRONMENTAL CRITERIA FOR SIX MUNITION COMPOUNDS

The interim criteria for the protection of human health and environment shown in Table 11.9 were calculated using essentially the methodologies proposed in the Federal Register by the USEPA (Barkley 1982). Currently, these criteria are being reviewed and updated by the Chemical Effects Information Task Group of the Oak Ridge National Laboratory for USAMBRDL using revised versions of the USEPA guidelines. This project will also identify research need- connected with the calculation of the environmental criteria. Criteria for HMX have not been established because of lack of data.

TABLE 11.9 RECOMMENDED INTERIM ENVIRONMENTAL CRITERIA FOR SIX MUNITION COMPOUNDS[a]

Compound	Criteria
Nitrocellulose	No criteria because of lack of toxicity at concentrations as high as 1000 mg/L
White Phosphorus	<0.01 μg/L (aquatic organisms)
Trinitroglycerin (nitroglycerin)	<10 μg/L (aquatic organisms)
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	33.68 μg/L (human exposure); 200 μg/L (aquatic organisms)
2,4,6-Trinitrotoluene (TNT)	<60 μg/L (aquatic organisms); (insufficient data)
2,4,-Dinitrotoluene(DNT)	62 μg/L (aquatic organisms)

a. Adapted from Barkley 1982.

11.7 PROPOSED WATER QUALITY STANDARDS FOR EFFLUENTS FROM THE AAPs

The water quality standards for effluents from the AAPs as proposed by the Ammunition Procurement and Supply Agency are given in Table 11.10. These data were published by Neal in 1973 and probably need to be revised and updated. It is interesting to note that the total concentration of nitrobodies in effluent and at boundary have been set by Neal at 0.5 and 0.3 mg/L, respectively. The criterion set by Barkley (1982) (see Section 11.6) for total nitrobodies amounts to 0.366 mg/L in the effluent.

USEPA (1984b, 1984c) effluent guidelines for explosive manufacture and for load, assemble, and pack plants are given in Table 11.11 and 11.12, respectively. The former is applicable to the manufacture of dynamite, nitroglycerin, RDX, HMX, and TNT. According to USEPA, these effluent limitations and guidelines represent the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

TABLE 11.10. PROPOSED APSA[a] WATER QUALITY STANDARDS FOR EFFLUENTS FROM AAPs[b]

Pollutant [ppm (mg/L), except as noted]	APSA Standard	
	Effluent	Boundary
Aluminum	1.0	0.1
Ammonia	0.1	0.01
Antimony	0.05	0.01
Arsenic	0.05	0.01
Barium	1.0	0.1
Beryllium	0.05	0.01
Bicarbonate	35	35
Bismuth	1.0	0.5
Boron	1.0	0.1
Bromide	1.0	0.5
Cadmium	0.01	0.01
Calcium	100	50
Cesium	1.0	0.1
Chloride	150	25
Chromium (hexavalent)	0.05	0.05
Chromium (trivalent)	1.0	1.0
Cobalt	1.0	0.1
Copper	0.2	0.02
Cyanide	0.025	0.01
Fluoride	10	0.7
Germanium	0.5	0.05
Iron	0.3	0.05
Lanthanum	1.0	0.1
Lead	0.05	0.01
Lithium	0.5	0.1
Magnesium	30	15
Manganese	0.05	0.01
Mercury	0.01	0.01
Molybdenum	1.0	0.1
Nickel	1.0	0.1
Nitrate	5.0	0.5
Nitrogen (Kjeldahl)		
Phosphate	0.5	0.05
Platinum	0.5	0.05
Potassium	10	10
Radioactivity (total)	(c)	(c)
Selenium	0.01	0.01
Silicon Oxide	6	6
Silver	0.05	0.01
Sodium	100	10-60
Strontium	10	0.1
Sulfate	200	50

TABLE 11.10. (Continued)

Pollutant [ppm (mg/L), except as noted]	APSA Standard	
	Effluent	Boundary
Sulfite	2.0	0.1
Tantalum	1.0	0.1
Tellurium	0.1	0.1
Thorium	1.0	0.1
Tin	1.0	0.1
Titanium	1.0	0.1
Tungsten	1.0	0.1
Uranium	1.0	0.1
Uranyl ion		
Vanadium	0.5	0.1
Zinc	0.5	0.05
Zirconium	1.0	0.1
Total heavy metal	5.0	5.0
Bacteria-monthly average (No./100 mL)-% of samples (Coliform count)		(5000)-20 (2000)-5
Biological oxygen demand	15	2.0
Carbon (chloroform extract)		
Color (color, Pt-Co, units)	3-30	3-30
Chemical oxygen demand	20	2.0
Herbicides	0.0001	0.0001
Insecticides carbamate	0.0005	0.0001
Insecticides chlorinated hydrocarbons	0	0
Insecticides organic phosphorous	0.0005	0.0001
Maximum temperature (°F)	raise <5, 1°/hr rate	90
Methylene blue (active substances)		
Oil	15	No visible oil on water surface
Oxygen, dissolved (minimum value)	5.0	5.0
pH (pH units)	6.0-8.5	6.0-8.5
Phenols	0.01	0.01
Solids, dissolved (total)	500	200
Solids, settleable		
TNT and nitrobodies	0.5	0.3
Total organic carbon	30	3.0
Turbidity		

a. APSA = Ammunition Procurement and Supply Agency

b. Adapted from Neal 1973.

c. Radioactivity - gross beta activity in the known absence of ^{90}Sr and alpha emitters not to exceed nCi per liter at any time. "Absence of" is defined as not more than 10 pCi ^{90}Sr and 3 pCi of alpha radiation.

TABLE 11.11. EFFLUENT LIMITATIONS FROM THE MANUFACTURE OF DYNAMITE, NITROGLYCERIN, RDX, HMX, AND TNT[a]

Effluent Characteristic[c]	Effluent limitations[b]	
	Daily Maximum	30-Day Average
COD	7.77	2.59
BOD_5	0.72	0.24
TSS	0.25	0.084
pH	6.0-9.0	6.0-9.0

a. Adapted from USEPA 1984c.

b. 30-Day average is average of daily values for 30 consecutive days.

c. COD = chemical oxygen demand; BOD_5 = biochemical oxygen demand, 5 days; TSS = total suspended solids.

TABLE 11.12. EFFLUENT LIMITATIONS FROM THE LOAD, ASSEMBLE, AND PACK OPERATION PLANTS[a]

Effluent Characteristic	Effluent limitations[b]	
	Daily Maximum	30-Day Average
Oil and grease	0.11	0.035
Total suspended solids	0.26	0.088
pH	6.0-9.0	6.0-9.0

a. Adapted from USEPA 1984b.

b. Metric units - kg/ 1000 kg of product;
English units - lb/1000 lb of product.

12. LITERATURE CITED

Abelson, P.H. 1984. Effects of SO_2 and NO_x emissions. Science 226:1263.

Andrews, C. 1982. Treatment of explosives and pyrotechnic wastes at NAVWPNSUPPCEN, Crane. In: J.A.E. Hannum, ed. Hazardous Waste Management (Propellants and Related Items). pp. 69-83. S&EPS Workshop, Redstone Arsenal, AL, October 19-21 1982.

Bane, J. M., M. D. Luh, D. J. Freeman, and A. A. Carotti. 1977. Abatement of Sulfate Pollution at Newport Army Ammunition Plant. Final Report, AD-E400 038. Process Technology Branch, Edgewood Arsenal, Aberdeen Proving Ground, MD. 92 pp.

Barkley, Jr., J. J. 1982. Recommended Interim Environmental Criteria for Six Munition Compounds. U.S. Army Biomedical Research and Development Command, Ft. Detrick, MD.

Bender, E. S., V. J. Kelmeckis, P. F. Robinson, D. D. Rieder, and R. J. Donald. 1977a. Preliminary Environmental Survey of Volunteer Army Ammunition Plant, Tyner, Tennessee, March 1976. Technical Report, 77016, AD-A043 662. U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD. 83 pp.

Bender, E. S., P. F. Robinson, M. W. Moore, W. D. Thornton, and A. E. Asaki. 1977b. Preliminary Environmental Survey of Holston Army Ammunition Plant, Kingsport, Tennessee, April 1976. Technical Report, 77053, AD-A041 897. U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD. 76 pp.

Bentley, R. E., G. A. LeBlanc, T. A. Hollister, and B. H. Sleight. 1977. Laboratory Evaluation of the Toxicity of Nitrocellulose to Aquatic Organisms. Final Report, AD A037749. EG&G Bionomics, Wareham, MA. DAMD-17-14-C-4101. 34 pp.

Blaylock, B. J., J. S. Santos, and B. Jackson, Jr. 1976. Pollution Status Report, Milan Army Ammunition Plant. Technical Report, 4932. Martin Marietta Aluminum Sales, Inc., Milan, TN. 32 pp.

Bolleter, W. T. 1971. Joint US/UK Seminar on TNT Chemistry and Manufacture, 26th October. Explosives Research and Development Establishment (UK) Technical Report No. 106, pp. 3-45.

Bolleter, W. T. 1985. Personal communication to B. C. Pal concerning Radford Army Ammunition Plant.

Bolleter, W. T. 1977. Recent improvements in the continuous TNT manufacturing process. Symposium on Processing Propellants, Explosives and Ingredients, Naval Postgraduate School, Monteray, CA.

Brundege, J. A., L. Silberman, and J. Dowden. 1982. Alternate Processes for the Treatment and Disposal of Spent Acid Sludge from RDX/HMX Manufacture. Final Report, AD-B065 463. Hayes, Seay, Matten, and Matten. Roanoke, VA. DAAK10-S1-C-0015. 29 pp.

Cali, L. 1985. Personal communication concerning details of environmental problems and pollution treatment at Radford Army mmunition Plant.

Carpenter, B. H., R. Liepins, J. Sickles, H. L. Hamilton, D. W. VanOsdell, G. E. Weant, and L. W. Worsham. 1978a. Specific Air Pollutants from Munitions Processing and Their Atmospheric Behavior. Vol. 1. Executive Summary and General Appendices. Final Report, AD-A060 354. Research Triangle Institute, Research Triangle Park, NC. DAMD17-76-C-6067.

Carpenter, B. H., R. Liepins, J. Sickles, H. L. Hamilton, D. W. VanOsdell, G. E. Weant, and L. W. Worsham. 1978b. Specific Air Pollutants from Munitions Processing and Their Atmospheric Behavior. Vol. 2. RDX/HMX Production. Final Report, AD-A060 122. Research Triangle Institute, Research Triangle Park, NC. DAMD17-76-C-6067.

Carpenter, B. H., R. Liepins, J. Sickles, H. L. Hamilton, D. W. VanOsdell, G. E. Weant, and L. W. Worsham. 1978c. Specific Air Pollutants from Munitions Processing and Their Atmospheric Behavior. Vol. 3, TNT Production. Final Report, AD-A060 147. Research Triangle Institute, Research Triangle Park, NC. DAMD17-76-C-6067.

Carpenter, B. H., R. Liepins, J. Sickles, H. L. Hamilton, D. W. VanOsdell, G. E. Weant, and L. W. Worsham. 1978d. Specific Air Pollutants from Munitions Processing and Their Atmospheric Behavior. Vol. 4. Open Burning and Incineration of Waste Munitions, Final Report, AD-A060 155. Research Triangle Institute, Research Triangle Park, NC. DAMD17-76-C-6067.

Carrazza, J. A. 1983. Pollution abatement and environmental control technology program. control concepts for nitramines and nitroguanidine. In: Unpublished proceedings of DARCOM Environmental Qualtiy R&D Symposium.

Carrazza, J., E. Pregun, C. Chandler, and W. Helbert. 1984. Treatment of wastewater (red water) resulting from TNT purification. In: Proceedings of the 13th Environmental Systmes Symposium, Bethesda, MD., March 20-22. American Defense Preparedness Association. pp. 174-204.

Chandler, C. D. and W. B. Helbert, Jr. 1980. Elimination of NO_x in Process Tail Gas from TNT Manufacture by Absorption in Sulfuric Acid. Final Engineering Report on Production Engineering Project PE-352, Phase II, Radford Army Ammunition Plant, Hercules, Inc., Radford, VA. DAAA09-77-4007. 14 pp.

Chandler, C. D., J. A. Kohlbeck, and W. T. Bolleter. 1972. Continuous trintrotoluene process studies. IV. Identification and determination of purification byproducts. J. Chromat. 67:255-259.

Chemical Engineering News. 1984. Hazardous waste furnaces to be developed. Chem. & Eng. News, August 13, p. 9.

Chen, T. H., C. Campbell, and W. J. Fisco. 1981. Characterization of Pollutants at Holston Army Ammunition Plant. Technical Report, ARLCD-TR-81035. AD A107340. U.S. Army Armament Research and Development Command, Large Caliber Weapon Systems Laboratory, Dover, NJ.

Clayton, G. D. and F. E. Clayton, eds. 1981. Patty: Industrial Hygiene and Technology, 3rd ed, Vols. IIa, IIb. Interscience Publishers, New York.

Clayton, G. D. and F. E. Clayton, eds. 1982. Patty: Industrial Hygiene and Technology, 3rd ed., Vol. IIc. Interscience Publishers, New York.

Clear, J. and P. Collins. 1982. Contamination Survey Iowa Army Ammunition Plant. Final Report, DRXTH-AS-CR-82137. Environmental Research Group, Inc. Ann Arbor, MI. DAAA09-78-C-3008. 150 pp.

Cooper, D. C., M. A. Eischen, D. A. Holzworth, R. J. Jakobsen, B. E. Sherwood, J. M. Stilwell, and P. E. Strup. 1975. Aquatic Field Surveys at Badger, Joliet, and Lake City Army Ammunition Plants. Final Report, AD-B007 433L. Battelle Columbus Laboratories, Columbus, OH. DAMD-17-74-C-4133. 185 pp.

Copeland, L., H. R. Jowers, L. Sotsky, and J. A. Carrazza. 1983. In-Plant Reuse of Pollution Abated Waters, Phase I. Milan AAP. Final Report, AD-B072 952L. Martin Marietta Aluminum Sales, Inc., Milan, TN. DAAA09-77-C-4002. 66 pp.

Department of Energy. 1983. NO_x Information Book. DOE/NBB-0044. NTIS.

Dacre, J. and D. H. Rosenblatt. 1974. Mammalian Toxicology and Toxicity to Aquatic Organisms of Four Important Types of Waterborne Munitions Pollutants - An Extensive Literature Evaluation. Technical Report, 7403, AD-778725. U.S. Army Medical Bioengineering Research and Development Laboratory, Aberdeen Proving Ground, MD. 187 pp.

Emerson, R. D. 1985. Personal communication during review process, August 21, 1985, from Civilian Executive Assistant at Holston Army Ammunition Plant.

Envirodyne Engineers, Inc. 1980. Milan Army Ammunition Plant Contamination Survey. Final Report, AD-B053362. Envirodyne Engineers, Inc., St. Louis, MO, J-79-669. 119 pp.

EPRI. 1982a. DOWA process demonstration. Final report, EPRI CS-2359. Electric Power Research Institute, Palo Alto, CA.

EPRI. 1982b. Status of Spray-dryer Flue Gas Desulfurizaton. Final Report, EPRI CS-2209. Electric Power Research Institute, Palo Alto, CA.

Etnier, E. L. 1985. Water Quality Criteria for Hexahydro-1,3,5-Trinitro-1,3,5-triazine (RDX). Draft Report, ORNL-6178. Chemical Effects Information Group, Oak Ridge National Laboratory, Oak Ridge, TN. PO 84 PP4845. 156 pp.

Evans, J. R. 1984. Personal communication during site visit to Holston Army Ammuntion Plant on July 16-17, 1984. Included datasheets for NPDES monitoring.

Farber, P. S. 1976. Control of nitrogen oxide emissions from TNT plants. In: L. Theodore, E. J. Rolinski, W. N. McCarthy, Jr., A. J. Buonicore, D. E. Earley, and R. A. Servais, eds. Proceedings of the 4th National Conference on Energy and the Environment, Cincinnati, OH.

Fedoroff, B. T., H. A. Aaronson, O. E. Sheffield, E. F. Reese, and G. D. Clift. 1960a. Encyclopedia of Explosives and Related Items, Vol. 1. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T., H. A. Aaronson, O. E. Sheffield, E. F. Reese, and G. D. Clift. 1960b. SEX and TAX. In: Encyclopedia of Explosives and Related Items, Vol. 1, pp. A49-A50. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1962a. Cellulose nitrates or nitrocellulose. In: Encyclopedia of Explosives and Related Items, Vol. 2, pp. C100-125. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1966a. Cyclotetramethylenetetranitramine. In: Encyclopedia of Explosives and Related Items, Vol. 3, pp. C605-610. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1962b. Encyclopedia of Explosives and Related Items, Vol. 2. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1966b. Encyclopedia of Explosives and Related Items, Vol. 3. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1969. Encyclopedia of Explosives and Related Items, Vol. 4. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1972a. Encyclopedia of Explosives and Related Items, Vol. 5. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1974a. Encyclopedia of Explosives and Related Items, Vol. 6. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1974b. Glycerol trinitrate or nitroglycerin (NG). In: Encyclopedia of Explosives and Related Items, Vol. 6, p. G-98. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T., O. E. Sheffield, and S. M. Kaye. 1975. Encyclopedia of Explosives and Related Items, Vol. 7. Picatinny Arsenal, Dover, NJ.

Fedoroff, B. T. and O. E. Sheffield. 1972. Nitroglycerin (NG) or glycerol trinitrate. In: Encyclopedia of Explosives and Related Items, Vol. 5, pp. D1593-D1594. Picatinny Arsenal, Dover, NJ.

Fischer, G., L. Sotsky, and J. A. Carrazza. 1982. In-Plant Reuse of Pollution Abated Waters at Kansas Army Ammunition Plant. Phase I. Feasibility Study, Final Report, AD-B062 730. Day & Zimmermann, Inc., Parsons, KS. DAAA09-76-C-4021. 38 pp.

Fischer, G., L. Sotsky, and J. A. Carrazza. 1983. In-Plant Reuse of Pollution Abated Waters. Phase II. Kansas Army Ammunition Plant. Final Report, AD-B074 672. Day & Zimmermann, Inc. Parsons, KS. DAAA09-76-C-4021. 59 pp.

Forsten, I. 1980. Disposal of Hazardous Toxic Munition Waste. Natl. Conf. Environ. Eng. Proc. ASCE Environ. Eng. Div. Spec. Conf., 1980:440-452.

Fowler, E. B. 1965. A Study of the Biological Degradation of TNT and its Application to the Disposal of TNT Wastewaters. Draft report of work by Los Alamos Scientific Laboratory Group 4-7.

Ghassemi, M., J. Santos, and B. Jackson, Jr. 1976. Report on In-Depth Pollution Survey at Joliet Army Ammunition Plant. Technical Report, 4941, AD-B011 415L. Picatinny Arsenal, Dover, NJ. 132 pp.

Gilbert, E. E. 1980. TNT. In: S. M. Kaye, ed. Encyclopedia of Explosives and Related Items, Vol. 9, pp. T235-T286. U.S. Army Armament Research and Development Command, Dover, NJ.

Gilbert, E. E., V. I. Siele, C. D. Chandler, R. A. Mundy, J. R. Spencer, G. R. Gibson, and W. T. Bolleter. 1982. New procedures for purifying TNT. Propellants, Explosives, Pyrotechnics. 7:150-154.

Griffin, W. R., J. S. Santos, and B. Jackson, Jr. 1976. Pollution Status Report, Lone Star Army Ammunition Plant. Technical Report 4956. Day & Zimmermann, Inc., Texarkana, TX. 35 pp.

Hale V. Q., T. B. Stanford, and L. G. Taft. 1979. Evaluation of the Environmental Fate of Munition Compounds in Soil. Final Report, AD-A082874. Battelle Columbus Laboratories, Columbus, OH. DAMD17-76-C-6065.

Hammer, F. T. 1982. Contamination Survey for the Iowa Army Ammunition Plant (IAAP). Final Report, AD-B074 315L. Mason Hanger-Silas Mason Company, Middletown, IA. AAA09-78-C-3008.

Hash, R. L., J. R. Evans, and P. V. Simmerly. 1977. Pilot Plant Investigation for Treatment of Explosive Contaminated Wastewater from Holston Army Ammunition Plant. Technical Report No. HDC-32-77, Holston Defense Corporation, Kingsport, TN.

Hauze, R. C., J. S. Santos, and B. Jackson, Jr. 1977. Pollution Status Report Volunteer Army Ammunition Plant. Technical Report 4998. ICI-United States, Inc., Chattanooga, TN. 152 pp.

Heffinger, J. G. 1984. River Survey Within the Boundary of Radford Army Ammunition Plant. Final Engineering Report, PE-723. Hercules Incorporated, Radford Army Ammunition Plant, Radford, VA. 90 pp.

Heffinger, Jr. J. G. and E. Pregun. 1985. Evaluation of Pollution Characteristics of Nitramine Propellant Wastewaters. Final Report, AD-B090505L. Hercules Incorporated, Radford Army Ammunition Plant, Radford, VA. 75 PP.

Helbert, Jr., W. B. and H. L. Stull. 1984. Red Water Pollution Abatement System. Final Report, AD-B082717. Hercules, Inc., Radford, VA. DAAA09-77-C-4007. 56 pp.

Hercules. 1984a. Radford Army Ammunition Plant, Future Pollution Abatement R&D Requirements. Hercules, Inc., Radford, VA. 15 pp.

Hercules. 1984b. Volatile Organic Carbon Emissions. Interim letter report, process engineering project PE-694.

Hoffsommer, J. C., L. A. Kaplan, D. J. Glover, D. A. Kubose, C. Dickinson, H. Goya, E. G. Kayser, C. L. Groves, and M. E. Sitzmann. 1978. Biodegradability of TNT: A Three-year Pilot Plant Study. Final Report, NSWC/WOL TR77-136, AD A061144. Naval Surface Weapons Center, White Oak, Silver Springs, MD.

Huff, B. L., W. D. Duckert, P. G. Barding, J. H. Wheeler, and R. B. Bogardus. 1975a. Aquatic Field Surveys at Radford, Holston, Volunteer, and Milan Army Ammuntion Plants. Volume I. Radford. Final Report, AD-A024 191. Wapora, Inc., Washington, DC. DAMD17-74-C-4138. 161 pp.

Huff, B. L., W. D. Duckert, P. G. Barding, J. H. Wheeler, and R. B. Bogardus. 1975b. Aquatic Field Surveys at Radford, Holston, Volunteer, and Milan Army Ammuntion Plants. Volume II. Holston. Final Report, AD-A024 191. Wapora, Inc., Washington, DC. DAMD17-74-C-4138. 143 pp.

Huff, B. L., W. D. Duckert, P. G. Barding, J. H. Wheeler, and R. B. Bogardus. 1975c. Aquatic Field Surveys at Radford, Holston, Volunteer, and Milan Army Ammuntion Plants. Volume III. Volunteer. Final Report, AD-A024 193. Wapora, Inc., Washington, DC. DAMD17-74-C-4138. 150 pp.

Huibregste, K. R., R. Fulk, A. E. Zanoni, and D. Zenkler. 1976. Feasibility Study Regarding Landfill of Nitrocellulose Lime Sludge and Oxidation of Nitroglycerin Wastewater Stream. Technical Report. Envirex Company, Milwaukee, WI. DAAG53-76-C-0082. 100 pp.

Innes, W. B. 1984. Nitric and sulfuric acid. Chem. and Eng. News, Oct. 15.

Isbister, J. D., R. C. Doyle, and J. F. Kitchens. 1980. Engineering and Development Support of General Decon Technology for the DARCOM Installation Restoration Program. Task 6 - Adapted/Mutant Biological Treatment. Phase I - Literature Review. Final Report, AD A110389. Atlantic Research Corporation, Alexandria, VA. DAAK11-80-C-0027.

Jackson, Jr., B. and J. M. Lachowski. 1984. Alternative Treatment Methods for Pink Water. Final Report, AD-B073 648L. ARRADCOM, LCWSL. Dover, NJ. 38 pp.

Jerger, D. E., P. B. Simon, R. L. Weitzel, and J. E. Schenk. 1976. Aquatic Field Surveys at Iowa, Radford, and Joliet Army Ammunition Plants. Volume III. Microbiological Investigation, Iowa and Joliet Army Ammunition Plants. Final Report, AD A036 778. Environmental Control Technology Corporation, Ann Arbor, MI. DAMD17-75-C-5046. 153 pp.

Justus, F. L. 1985. Personal communication concerning details of environmental problems and pollution treatment at Hawthorne Army Ammunition Plant.

Kaplan, D. 1983a. Biodegradation of munition compounds. In: Unpublished Proceedings of DARCOM Environmental Quality R&D Symposium, June 14-16. U.S. Army Materiel Development and Readiness Command.

Kaplan, D. 1983b. Biodegradation of nitrate esters. In: Unpublished Proceedings of DARCOM Environmental Quality R&D Symposium, June 14-16. U.S. Army Materiel Development and Readiness Command.

Kaplan, D. L. 1984. Personal communication to B. C. Pal.

Kaplan, D. L., J. H. Cornell, and A. M. Kaplan. 1982. Decomposition of nitroguanidine. Enviro. Sci. Tech. 16:488-492.

Kaplan, D. L. and A. M. Kaplan. 1985a. Degradation of Nitroguanidine in Soils. Final Report, NATRICK/TR-85/407. U.S. Army Natrick R&D Center, Natrick MA.

Kaplan, D. L. and A. M. Kaplan. 1985b. Biodegradation of N-dinitrosodimethylamine in aqueous and soil systems. Appl. Environ. Microbiol., in press.

Kaplan, D. L. and A. M. Kaplan. 1982. Thermophilic biotransformations of 2,4,6-trinitrotoluene under simulated composting conditions. Appl. Environ. Microbiol. 44:757-760.

Kaye, S. M. 1978. Encyclopedia of Explosives and Related Items, Vol. 9. U.S. Army Reserarch and Development Command, Dover, NJ.

Kaye, S. M. 1980a. Encyclopedia of Explosives and Related Items, Vol. 9. U.S. Army Reserarch and Development Command, Dover, NJ.

Kaye, S. M. 1983. Encyclopedia of Explosives and Related Items, Vol. 10. U.S. Army Reserarch and Development Command, Dover, NJ.

Kaye, S. M. 1980b. Solubility tables. In: Encyclopedia of Explosives and Related Items, Vol. 9, p. S156. U.S. Army Reserarch and Development Command, Dover, NJ.

Keirn, M. A., C. L. Stratton, J. J. Mousa, J. D. Bonds, D. L. Winegardner, H. S. Prentice, W. D. Adams, and V. J. Powell. 1981. Environmental Survey of Alabama Army Ammunition Plant. Final Report, AD B059961L. Environmental Science and Engineering, Inc., Gainesville, FL. DAAK11-79-C--131. 343 pp.

Kitchens, J. F., W. E. Harvard, D. M. Lauter, R. S. Wentsel, and R. S. Valentine. 1978. Preliminary Problem Definition Study of 48 Munitions-Related Chemicals, I. Explosives Related Chemicals. Final Report, AD 066 307. Atlantic Research Corporation, Alexandria, VA. DAMD17-77-C-7057. 293 pp.

Klausmeier, R. E. 1978. The Science Behind Composting of Explosives. Presented at the Safety, Pollution, Abatement, and Conservation of Energy Review (SPACER). U.S. Army Armament Research and Development Command, Dover, NJ.

Klausmeier, R. E., E. I Jamison, and T. Tatyrek. 1982. Composting of TNT: Airborne Products and Toxicity. Final Report, AD B063 383. Naval Weapons Support Center, Crane, IN.

Lauwreys, R. R. 1983. Industrial Chemical Exposure: Guidelines for Biological Monitoring. Biomedical Publications, David, CA.

Lindner, V. 1980. Explosives. In: R. E. Kirk and P. F. Othmer, eds., Encyclopedia of Chemical Technology, 3rd ed., Vol. 9, pp. 561-671. John Wiley and Sons, New York.

Luh, M. D. and J. M. Szachta. 1978. Evaluation of Industrial Liquid Waste Treatment Facilities/Processes at Radford Army Ammunition Plant. Technical Report, ARCSL-TR-78015, AD-B027545. Chemical Systems Laboratory. Aberdeen Proving Ground, MD. 51 pp.

Lund, N. H. 1983a. Ground-water Monitoring Results for Holston Army Ammunition Plant (AAP), TN for April 1983. Letter to Commander U.S. Army Armament, Munitions, and Chemical Command, Rock Island, IL. 2 pp.

Lund, N. H. 1983b. Ground-water Monitoring Results for Holston Army Ammunition Plant (AAP), TN for July-August 1983. Letter to Commander U.S. Army Armament, Munitions, and Chemical Command, Rock Island, IL. 2 pp.

Lund, N. H. 1983c. Ground-water Monitoring Results for Holston Army Ammunition Plant (AAP), TN for May 1983. Letter to Commander U.S. Army Armament, Munitions, and Chemical Command, Rock Island, IL. 2 pp.

Lund, N. H. 1984. Ground-water Monitoring Results for Holston Army Ammunition Plant (AAP), TN for October 1983. Letter to Commander U.S. Army Armament, Munitions, and Chemical Command, Rock Island, IL. 2 pp.

Lund, N. H. 1983d. Ground-water Monitoring Results for Holston Army Ammunition Plant (AAP), TN for September-October 1982. Letter to Commander U.S. Army Armament, Munitions, and Chemical Command, Rock Island, IL. 3 pp.

Maley, D. 1985. Personal communication concerning details of environmental problems and pollution treatment processes at Longhorn Army Ammunition Plant.

Matherly, D. G. 1985. Personal communication concerning details of environmental problems and pollution treatment at Mississippi Army Ammunition Plant.

Mayberry, D., J. S. Santos, and B. Jackson, Jr. 1976. Pollution Status Report, Radford Army Ammunition Plant. Technical Report 4933. Hercules, Inc., Radford, VA. 62 pp.

Maybury, D. H. 1982. Explosives Disposal Operations at Radford Army Ammunition Plant. In: J.A.E. Hannum, ed. Hazardous Waste Management, Chemical Propulsion Information Agency Publication 364, The Johns Hopkins University, Applied Physics Laboratory, Laurel, MD.

McCormick, N. G., J. H. Cornell, and A. M. Kaplan. 1981. Biodegradation of hexahydro-1,3,5-triniro-1,3,5-trizaine. Appl. Environ. Microbiol. 42(5): 817-823.

McCormick, N. G., F. E. Feeherry, and H. S. Levinson. 1976. Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds. Appl. Environ. Microbiol. 31:949-958.

McDonnell, C. H. 1978. Trinitromethane and tetranitromethane. In Kaye, S. M., ed., Encyclopedia of Explosives and Related Items, Vol. 8, pp. M78-M85. U.S. Army Armament Research and Development Command, Dover, NJ.

Morehead, C. A. 1985. Personal communication concerning details of environmental problems and pollution treatment at Newport Army Ammunition Plant.

Nay, M. W., C. W. Randall, and P. H. King. 1974. Biological treatability of trinitrotoluene manufacturing water. Water Pollut. Control 46:485-497.

Neal, L. G. 1973. Water Quality Standards and Regulations Applicable to Army Ammunition Plants. Vol. II. Final Report, AD 907216L. TRW, Redondo Beach, CA. DAAA21-72-C-0625. 224 pp.

Novak, F. 1983. AAP operations requiring R&D support. In: DARCOM Environmental Quality R&D Symposium, June 14-16.

Oster, C. C. 1985. Personal communication concerning details of environmental problems and pollution treatment at Twin Cities Army Ammunition Plant.

Pal, B. C. 1984. Personal communication to B. C. Pal during site visit at Radford Army Ammunition Plant.

Patel, N., L. Sotsky, and J. A. Carrazza. 1983. In-Plant Reuse of Pollution Abated Waters, Phase I. Lone Star Army Ammunition Plant. Final Report, AD B072 846. Day & Zimmermann, Inc., Texarkana, TX. DAAA-09-79-C-3001.

Patterson, J., I. N. Shapira, J. Brown, W. Buckert, and J. Polson. 1976. State-of-the-art: Military Explosives and Propellants Production Industry. Vol. I-III. EPA-600/2-76-213-a-c. U.S. Environmental Protection Agency. Washington, DC.

Pereira, W. E., D. L. Short, D. B. Manigold, and P. K. Roscio. 1979. Isolation and characterization of TNT and its metabolites in groundwater by gas chromatograph-mass spectrometer-computer techniques. Bull. Environ. Contam. Toxicol. 21:554-562.

RCRA. 1976. Resource Conservation and Recovery Act. In: Environmental Statutes, 1982 Edition. Government Institutes, Inc., Rockville, MD. pp. 399-457.

Ribaudo, C., C. Campbell, S. Bulusu, W. Fisco, T. Chen, H. Kramer, and T. Castorina. 1981. The Chemical Characterization of Pollutants in Wastewater from Volunteer Army Ammunition Plant. Report, AD-A105 705. U.S. Army Armament Research and Development Command, Large Caliber Weapon Systems Laboratory, Dover, NJ. DA1T762720D048.

Renard, D. E. 1985. Personal communication from Mr. David E. Renard of the U. S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.

Renard, D. E. 1984. Unpublished material obtained through the courtesy of Mr. David E. Renard of the U. S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.

Roth, J. 1980. RDX. In: S. M. Kaye, ed., Encyclopedia of Explosives and Related Items, Vol. 9, pp. R120-146. U.S. Army Armament Research and Development Command, Dover, NJ.

Ryon, M. G. 1985. Water Quality Criteria for Nitrocellulose. Draft Report, ORNL-6179. Chemical Effects Information Group, Oak Ridge National Laboratory. Oak Ridge, TN. PO84PP4845. 54 pp.

Saffian, L. W. 1985. Personal communication from D. L. W. Saffian, Energetic Systems, LAWSL, U.S. Army Armament Research and Development Center, Dover, NJ.

Sandrin, J. A. 1982. Open burning/open detonation of waste explosives. In: J. A. E. Hannum, ed. Hazardous Waste Management, Chemical Propulsion Information Agency Publication 364, The John Hopkins University, Applied Physics Laboratory, Laurel, MD.

Sanocki, S. L., P. B. Simon, R. L. Weitzel, D. E. Jerger, and J. E. Schenk. 1976. Aquatic Field Surveys at Iowa, Radford, and Joliet Army Ammunition Plants. Volume I. Iowa Army Ammunition Plant. Final Report, AD-DAMD17-75-C-5046. 418 pp.

Schroeder, W. A., P. E. Wilcox, K. N. Trueblood, and A. O. Dekker. 1951. Ultraviolet and visible absorption spectra in ethyl alcohol. Anal. Chem 23:1740-1747.

Schultz, T. J. 1982. Application of conventional incineration technology to propellant/explosive contaminated sludges. In: Hazardous Waste Management, ed. J. A. E. Hannum. CPIA Publication 364. The John Hopkins University, Applied Physics Laboratory, Laurel, MD.

Shabecoff, P. 1985a. Acid rain attacks environment beyond northeast. The New York Times, January 29.

Shabecoff, P. 1985b. E.P.A. asks overhaul of rules to speed toxic waste cleanup. The New York Times, January 29.

Shabecoff, P. 1985c. Gaps seen in data on burning toxic wastes. The New York Times, January 17.

Shabecoff, P. 1985d. High costs for military seen in waste cleanup. The New York Times, February 28.

Shapira, N. I., J. Patterson, J. Brown, and K. Noll. 1978. State-of-the-Art Study: Demilitarization of Conventional Munitions. EPA-600/2-78-012. American Defense Preparedness Assoication. Washington, DC. 126 pp.

Simon, R. L., R. A. Flores, and D. S. Ross. 1977. Oxidation Control in TNT Production. Final Report, AD-A048256. SRI International, Menlo Park, CA. DAAA21-77-C-0057. 21pp.

Slemrod, S. 1970. Producing TNT by Continuous Nitration. Ordn (March-April 1970) 525. (As cited in Gilbert 1980).

Smith, J. G. 1985. Water Quality Criteria for Nitroglycerin. Draft Report, ORNL-6179. Chemical Effects Information Group, Oak Ridge National Laboratory. Oak Ridge, TN. PO84PP4845.

Smith, L. L. 1984. Personal communication during site visit to Radford Army Ammunition Plant on July 18-19, 1984.

Smith, L. L., J. Carrazza, and K. Wong. 1982. Biological treatment for waste streams from propellants and explosives manufacturing. J. Hazard. Mat. 5:27-296.

Smith, L. L., J. Carrazza, and K. Wong. 1983. Treatment of wastewaters containing propellants and explosives. J. Hazard. Mat. 7:303-316.

Smith, L. L., T. D. Wheelock, A. F. Tatyrek, and J. A. Carrazza. 1983. Characterization and Treatment of Waste Water Sludges at Radford Army Ammunition Plant. Final Report, AD-B078453. Hercules, Inc., Radford, VA. DAAA09-77-C-4007.

Spanggord, R. J., B. W. Gibson, R. G. Keck, and G. W. Newell. 1978. Mammalian Toxicological Evaluation of TNT Wastewaters, Vol. 1. Chemistry Studies. Annual Report. SRI International, Menlo Park, CA. DAMD 17-76-C-6050, 332 pp.

Spanggord, R. J., T. Mill, T. -W. Chou, W. R. Mabey, and J. H. Smith. 1980. Environmental Fate Studies on Certain Munition Wastewater Constituents - Phase II, Laboratory Studies. Final Report, AD-A099 256. SRI International, Menlo Park, CA. 197 pp.

Stephan, C. E., D. I. Mount, D. J. Hansen, J. H. Gentile, G. A. Chapman, W. A. Bungs. 1985. Guidleines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses. Final Report, PB85-227049. U.S. Environmental Protection Agency, Washington, DC. 98 PP.

Stidham, B. R. 1979. Analysis of Wastewater for Organic Compounds Unique to RDX/HMX Manufacturing and Processing. Final Report, AD A085765. Holston Defense Corporation, Kingsport, TN. DAAA09-78-C-3000.

Stilwell, J. M., D. C. Cooper, M. A. Eischen, M. C. Matthews, B. E. Sherwood, and T. B. Stanford. 1976. Aquatic Life Field Studies at Joliet Army Ammunition Plant. Final Phase II, AD-A033 548. Battelle's Columbus Laboratories, Columbus, OH. DAMD17-74-C-4123.

Stull, H. L. 1984. Personal communication from Harvey L. Stull. Radford Army Ammunition Plant, Radford, VA.

Sullivan, J. H., Jr., H. D. Putnam, M. A. Keirn, B. C. Pruitt, Jr., J. C. Nichols, and J. T. McClave. 1979. A Summary and Evaluation of Aquatic Environmental Data in Relation to Establishing Water Quality Criteria for Munitions-Unique Compounds. Part 4: RDX and HMX, Final Report, AD-A087 683. Water and Air Research, Inc., Gainesville, FL. DAMD-77-C-7207. 71 pp.

Sullivan, J. H., Jr., H. D. Putnam, M. A. Keirn, D. R. Swift, and B. C. Pruitt, Jr. 1977. Aquatic Field Survey at Volunteer Army Ammunition Plant, Chattanooga, Tennessee. Final Report, AD-A042 590. Water and Air Research, Inc., Gainesville, FL. DAMD17-75-C-5049. 318 pp.

Sundaram, T. R., J. E. Santo, and A. F. Tatyrek. 1981. Hydroperm Microfiltration System for Treatment of TNT Pink Wastewater, Part I, No Pretreatment. Report ADB056940L. U.S. Army Armament Research and Development Command. 70 pp.

Talmon, Jr., W. B., J. S. Santos, and B. Jackson, Jr. 1976. Pollution Status Report, Cornhusker Army Ammunition Plant, Final Report, AD-B015 799. Mason and Hanger, Silas-Mason Co., Inc., Grand Island, NE. 114 pp.

Tatyrek, A. F. 1983. Detonator and Primer Waste Assessment Sources and Treatment Alternatives. Technical Report, AD-B078 444. U.S. Army Armament Research and Development Center, Dover, NJ. 33 pp.

TDB. 1982. Toxicology Data Bank. Trinitrotoluene. National Library of Medicine: MEDLARS, File TDB.

Traxler, R. W. 1975. Biodegradation of Trinitrotoluene (-TNT) and its Production Isomers. Annual Report, AD A029346. University of Rhode Island, Kingston, R.I. DAAG17-73-C-0276.

Urbanski, T. 1983a. Chemistry and Technology of Explosives, Vol. 1, Pergamon Press, New York.

Urbanski, T. 1983b. Chemistry and Technology of Explosives, Vol. 1, p. 589. Pergamon Press, New York.

Urbanski, T. 1983c. Chemistry and Technology of Explosives, Vol. 2, Pergamon Press, New York.

Urbanski, T. 1983d. Chemistry and Technology of Explosives, Vol. 2, pp. 32-61. Pergamon Press, New York.

Urbanski, T. 1983e. Chemistry and Technology of Explosives, Vol. 3, Pergamon Press, New York.

Urbanski, T. 1984. Chemistry and Technology of Explosives, Vol. 4, Pergamon Press, New York.

USAEHA. 1979. Water Quality Engineering Study 32-24-01800-79, Industrial Wastewater, Holston Army Ammunition Plant, Kingsport, TN. U.S. Army Environmental Hygiene AgencY. Aberdeen Proving Ground, MD.

USATHAMA 1984. Pollution Abatement and Environmental Control Technology Program-Pollution Abatement Program. U.S. Army Toxic and Hazardous Materials Agency.

USEPA. 1979b. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors-Third Edition, Supplement 9 (AP-42). National Technical Information System, Springfield, VA. PB81-244097.

USEPA. 1980a. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors-Third Edition, Supplement 10 (AP-42). National Technical Information System, Springfield, VA.

USEPA. 1980b. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors-Third Edition, Supplement 11 (AP-42). National Technical Information System, Springfield, VA. PB81-178014.

USEPA. 1981a. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors-Third Edition, Supplement 12 (AP-42). National Technical Information System, Springfield, VA.

USEPA. 1983a. U.S. Environmental Protection Agency. Compilation of Air Pollution Emission Factors, Third Edition, Supplement 14 (AP-42). National Technical Information System, Springfield, VA.

USEPA. 1984a. U.S. Environmental Protection Agency. Draft Report on Incineration of Hazardous Liquid Waste. Science Advisory Board, Environmental Effects, Transport and Fate Committee.

USEPA. 1984b. U.S. Environmental Protection Agency. Explosives load, assemble, and pack plants subcategory-effluent limitations and guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available. Fed. Reg.: 40 CFR 457.32.

USEPA. 1983b. U.S. Environmental Protecion Agency. Hazardous wastes from non-specific sources. Fed. Reg.: 40 CFR 261.31.

USEPA. 1983c. U.S. Environmental Protection Agency. Hazardous wastes from specific sources. Fed. Reg.: 40 CFR 261.32.

USEPA. 1981b. U.S. Environmental Protection Agency. Incinerator standards for owners and operators of hazardous waste management facilities; consolidated permit regulations. Fed. Reg.: 46 FR 7666.

USEPA. 1983d. U.S. Environmental Protection Agency. Incinerators. Fed. Reg.: 40 CFR 264.340.

USEPA. 1984c. U.S. Environmental Protection Agency. Manufacture of explosives subcategory-effluent limitations and guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available. Fed. Reg.: 40 CFR 457.12

USEPA. 1984d. U.S. Environmental Protection Agency. Open burning; waste explosives. Fed. Reg.: 40 CFR 265.382, Subpart P - Thermal Treatment.

USEPA. 1976. Quality Criteria for Water. Final Report, EPA-440/9-76-023. U.S. Environmental Protection Agency. Washington, DC. 501 pp.

USEPA. 1979ba. U.S. Environmental Protection Agency. Safe drinking water act. Fed. Reg.: 44 FR 42198.

USEPA. 1982a. U.S. Environmental Protection Agency. Standards applicable to owners and operators of hazardous treatment, storage and disposal facilities; consolidated permit regulations. Fed. Reg.: 47 FR 27516.

USEPA. 1983e. U.S. Environmental Protection Agency. Standards for owners and operators of hazardous waste treatment, storage, and disposal facilities. Fed. Reg.: 40 CFR 264.434.

USEPA. 1982b. U.S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Second Edition, Environmental Protection Agency, Washington, D.C.

VAPRC. 1983. Virginia Air Pollution Control Regulations. The Bureau of National Affairs Inc., Washington, DC.

Water and Air Research. 1976a. Water Quality Assessment for the Proposed RDX-HMX Facility. McAlester Naval Ammunition Depot, Volume I. Final Report, AD-A026 394. Water and Air Research, Inc., Gainesville, FL. DAMD-17-75-C-5049.

Water and Air Research. 1976b. Water Quality Assessment for the Proposed RDX-HMX Facility. Newport Army Ammunition Plant. Final Report, AD-A026 207. Water and Air Research, Inc., Gainesville, FL. DAMD-17-75-C-5049.

Weir, R. H., J. S. Santos, and B. Jackson, Jr. 1976. Pollution Status Report, Newport Army Ammunition Plant. Technical Report 4938. E. I. DuPont de Nemours and Co. Newport, IN. 27 pp.

Weitzel, R. L., P. B. Simon, D. E. Jerger, and J. E. Schenk. 1975. Aquatic Field Survey at Iowa Army Ammunition Plant. Final Report, AD-A014 300. Hercules, Inc., Cumberland, MD. DAAA21-73-C-0771. 152 pp.

Wendes, J. C. H. and J. R. Little. 1954. Report on the Known European Processes for the Continuous Production of Trinitrotoluene. Kanakee Unit, Joliet Ars. (As cited in Gilbert 1980).

Wendt, T. M., J. H. Cornell, and A. M. Kaplan. 1978. Microbial degradation of glycerol nitrates. Appl. Environ. Microbiol. 36:693-699.

Williams, R. J. P. 1984. Acid rain-why has there been no clear statement from British chemists? Chem in Britain 20(11):986.

Windholz, M. ed. 1976. The Merck Index. An Encyclopedia of Chemicals and Drugs. Merck and Company, Rahway, NJ.

Wood, J. D. 1982. Incineration of PEP Materials. In: J. A. E. Hannum, ed. Hazardous Waste Management, Chemical Propulsion Information Agency, Publication 364, The Johns Hopkins University, Applied Physics Laboratory, Laurel, MD.

Wood, J. D., S. P. Torrisi, D. R. Wright, W. A. White, and C. J. Staniec. 1981. Environmental Assessment: Decontamination/Cleanup Operations for the Leaseback Area of Alabama Army Ammunition Plant, Alabama. Final Report, AD-A114 896. U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD. 42 pp.

Yinon, J. and S. Zitrin. 1981. The Analysis of Explosives. Pergamon Press, New York.

Zeigler, J. P. 1980. The environmental aspects in the modernization of propellants/explosive plants. Pap. Jt. Symp. Compat. Plastics/Mater. Explos. Process. Explos. pp. 61-71.

13. GLOSSARY

AAP	Army Ammunition Plant
APSA	Ammunition Procurement and Supply Agency
AMCCOM	Army Armament Munitions and Chemical Command
CFR	Code of Federal Register
COD	Chemical oxygen demand
DEGDN	Diethylene glycol dinitrate
DNT	Dinitrotoluene
dpm	Disintegrations per minute
DSCF	Dry standard cubic feet
EAK	Ethylene diamine dinitrate, Ammonium nitrate, Potassium nitrate (plus aluminum powder)
FR	Federal Register
GAC	Granular activated carbon
GOCO	Government owned and contractor operated
GOGO	Government owned and government operated
gpm	Gallons per minute
HC	Hydrocarbon, organic material
LAP	Load, assemble, and pack
MHF	Multiple Hearth Furnace
MMT	Manufacturing Methods and Technology
MMTPAT	Manufacturing Methods and Technology Pollution Abatement Technology Program
MNT	Mononitrotoluene
Mg	Megagram, 10^6 gram
NPDES	National Pollution Discharge Elimination System

P&E	Propellants and explosives
PAECT	Pollution Abatement and Environmental Control Technology
PEP	Propellant, explosive, and pyrotechnic materials
ppm	Parts per million
RCRA	Resource Conservation and Recovery Act
SAR	Sulfuric Acid Recovery or Regeneration
SITPA	Simplified Incinerator Technology for Pollution Abatement
SRP	Sulfite Recovery Process
SSRP	Sodium Sulfite Recovery Plant
TNM	Tetranitromethane
TNT	α-Trinitrotoluene (unless mentioned otherwise)
USAMBRDL	U.S. Army Medical Bioengineering Research and Development Laboratory
USAPBMA	U.S. Army Production Base Modernization Agency
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency
VOC	Volatile organic compound

APPENDIX A

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Nitroguanidine Production Wastewater Treatment Technology

Intended User: Nitroguanidine production facility

II. DEFICIENCY/NEED THAT TASK ADDRESSES

The nitroguanidine production facility at Sunflower AAP currently does not have adequate facilities for treatment of wastewaters containing nitroguanidine and guanidine nitrate prior to discharge. Treatment technology must be developed, piloted, designed, and installed in order to achieve regulatory compliance during production (scheduled to begin in FY 1985).

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984 - Lab/bench scale development of selected treatment concepts.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1984 - Preparation/transfer of technical data package for advanced development pilot plant studies.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Treatment of Nitramine Propellant Production Wastewater

Intended User: Nitramine propellant production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

The effect of nitramine propellant production wastes on biological treatment systems for combined industrial operations waste control is unknown. Pretreatment requirements must be determined and developed before any large-scale production of nitramine propellants can be successfully performed.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-84 - Determination of the technical feasibility of utilizing existing biotreatment facilities.

FY 1985 - Pilot plant studies to develop necessary waste stream pretreatment technology and to verify physical/operational changes in existing combined waste treatment facilities.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Preparation/submittal of technical data package for design of pretreatment facility and for implementation of physical/operational changes in existing combined waste treatment facilities.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: RDX/HMX Production Wastewater Treatment System Evaluation/Optimization Study

Intended User: RDX/HMX production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

In 1974, a new Industrial Liquid Waste Treatment Plant was designed for Holston AAP that would have a broad range of operating capabilities. Installation of this facility is currently being completed. Complete data regarding necessary treatment conditions for RDX, HMX, and related production by-products were not existent at the time of design to ensure adequate and/or optimal operating conditions under current regulatory restraints. Optimum treatment conditions need to be determined for the Holston AAP facility and to provide an optimal design basis for new RDX/HMX production waste treatment facilities.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Characterization/measurement/evaluation of waste treatment facility as installed.

FY 1985 - Model evaluation (and verification by treatment system sampling and analysis) to determine optimum operating conditions for HMX/RDX production wastewater treatment.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Preparation/submittal of recommended optimum operating conditions for Holston AAP facility and operating changes to be incorporated in new production facility waste treatment system designs.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Treatment of Ball Powder Wastewater

Intended User: AMCCOM, Badger Ammunition Plant

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Badger AAP has the Army's only facility for manufacturing subject material. Currently inactive, Badger AAP has not operated since 1975, but it remains in the mobilization plan and can be expected to be reactivated in the future. Since the facility was last in production, regulatory discharge criteria have changed so that the wastewater treatment system formerly used is now completely inadequate to allow production in compliance with environmental regulations.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1983-85 - Biodegradation studies to determine chemistry and kinetics associated with biotreatment of individual contaminants as well as representative contaminant mixtures.

FY 1984-85 - Determination of most cost beneficial and technically acceptable treatment concept alternatives.

FY 1985-86 - Lab/bench studies to develop selected treatment concepts.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Preparation/transfer of exploratory development technical data package for advanced development at Badger AAP.

AD-A165 853 DATABASE ASSESSMENT OF POLLUTION CONTROL IN THE MILITARY EXPLOSIVES AND P..(U) OAK RIDGE NATIONAL LAB TN B C PAL ET AL. FEB 86 ORNL-6202 DE-AC05-85OR21400 3/3

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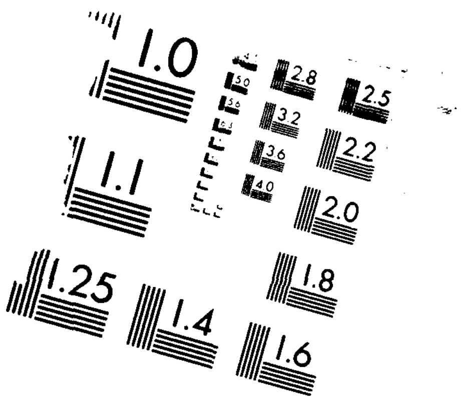

MICROCOPY RESOLUTION TEST CHART

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Propellant Production VOC Emissions Control

Intended User: Propellant manufacturing installation

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Propellant manufacturing plants must recover volatile organic solvents such as acetone and ethanol to comply with air pollution regulations as well as to reuse the solvents. Current state-of-the-art technology and commercial systems are not readily applicable because of the presence of explosively sensitive compounds along with the normal VOCs that are emitted. The adaptability of current technology (and whether new technology needs to be developed) is currently unknown.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Select best treatment process for development.

FY 1986 - Lab/bench scale development of selected process.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Preparation/transfer of technical data package for advanced development of pilot plant studies.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: DEGDN Wastewater Treatment Technology

Intended User: Radford AAP manufacturing facility

II. DEFICIENCY/NEED THAT TASK ADDRESSES

The wastewater generated from DEGDN propellant manufacture has a high nitrate content which will overload the combined waste treatment facility and cause a violation of environmental regulations when discharged. Treatment and reduction of the nitrate content are necessary to achieve regulatory compliance.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - A process is being developed wherein the wastewaters are neutralized and then heated to achieve denitration. The process is also being developed to reclaim remaining excess acid. Hazard analysis and elimination studies are being conducted concurrently.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985-86 - Preparation/transfer of technical data package for large-scale facility design at Radford AAP.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Nitrocellulose (NC) Fines Alternate Treatment Technology

Intended User: NC production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Current treatment technology is only acceptable for achieving regulatory compliance if production rate is low enough to allow use of lagoons without their overflow. If production would increase to or approach capacity at any NC facility, sufficient physical space would not be available for the number of lagoons required to operate in regulatory compliance. Alternate treatment technology is needed to be available to assure regulatory compliance if high production rates are required.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Evaluation of treatment technology alternatives; selection of best alternatives for development.

FY 1985-86 - Lab/bench scale development of selected alternative concepts.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Preparation/transfer of technical data package for advanced development pilot plant studies.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Granular Activated Carbon (GAC) System Pilot Optimization Study

Intended User: Pink water treatment facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Army Ammunition Plants and depots currently employ GAC treatment systems to meet nitrobody removal requirements of their NPDES permits. These GAC treatment systems were designed for low production levels and relatively high discharge limits. Performance data on GAC removal of nitrobodies such as DNT and RDX/HMX does not exist, and specific performance data on removal of nitrobodies to anticipated discharge standards for full capacity production are required to determine system modifications required to achieve regulatory compliance.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Granulated Activated Carbon System Pilot Optimization Study to determine optimum operating conditions and physical plant modifications.

FY 1985-86 - Demonstration of actual operational implementation; identification/resolution of field problems.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985-86 - Recommendations for optimum operating conditions transmitted to intended uses through command and subcommand channels for implementation.

FY 1986-87 - Distribution of results of field implementation/demonstration of actual operation; operational guidelines for system modification and optimum operations.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Nitrosamine Formation in Liquid Propellants (W-90)

Intended User: Liquid propellant production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

In the process of production triethanol ammonium nitrate (TEAN), a toxic impurity, N-nitrosodiethanolamine, is formed. Conditions affecting the formation of this impurity must be studied to determine how to reduce or eliminate it during the large-scale manufacture of TEAN. At this point any detectable level is considered both a potential hazard to manufacturing personnel and gun crews, and an environmental hazard unless adequate waste treatment is employed.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Liquid propellant synthesis study to determine process variables affecting nitrosamine formation (hazardous by-products formation)

FY 1985-86 - Liquid propellant synthesis optimization and storage stability studies.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Technical data package regarding optimum production and storage conditions for inclusion in product development package.

I. TASK DESCRIPTION

Title: Detonator Waste Treatment Technology Assessment

Intended User: Detonator production/loading facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Current treatment technology for control of wastewater generated from detonator loading and production operations is reportedly costly and has questionable capability for complete compliance with all applicable environmental regulations.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Determination of the justification for improved technology development based on cost-benefit analysis and assessment of existing technology deficiencies.

FY 1985-86 - If justified, selection of best alternatives/concepts to develop as improved technology.

FY 1986-87 - Lab/bench scale development phase.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Presentation of justification basis for appropriate command elements review/concurrence.

FY 1987 - Preparation/transfer of technical data package for advanced development pilot plant studies.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Sulfuric Acid Recovery Waste Disposal

Intended User: Army Ammunition Plant SAR facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

The manufacture of explosives at Army Ammunition Plants requires the production of large quantities of nitric and sulfuric acids. The nitric acid becomes part of the explosive molecule, but the sulfuric acid provides only a reaction medium and catalytic effect and is therefore recovered and reused. Sulfuric Acid Recovery (SAR) units discharge an acidic wastewater, which is currently treated by lime neutralization and lagooning, which involves subsequent production of large quantities of sludge. The lagoons represent a potential groundwater contamination source and must be cleaned frequently to remove the sludge which is regulated as a hazardous waste. Many facilities are also reportedly experiencing poor water clarification.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1985-86 - Assessment of current technology deficiencies and evaluation of improved treatment alternatives.

FY 1986-87 - Lab/bench development of selected improved treatment technology concepts.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Publication of recommended new treatment technologies to be developed for appropriate command elements review/concurrence.

FY 1987 - Preparation/transfer of technical data package for advanced development pilot studies.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Alternate Technologies Evaluations

Intended User: Applicable AMC industrial operation waste treatment facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Control treatment technology development is a large volume industry in the private sector. As a result, the state of the art is continually being improved to provide more cost-effective and technically efficient means for treating different operational wastes. The results of this development need to be evaluated periodically in order to identify applicable commercial systems that could be employed in AMC industrial operations to reduce operational costs and prevent unnecessary internal development efforts.

III. TECHNOLOGY DEVELOPMENT PLAN

F 1985-86 - Review/evaluate commercial state of the art related to catalytical conversion, thermo-, ultrasonic and microwave degradation treatment systems as well as microprocessor control systems for applicability as more cost-effective technology for pertinent AMC industrial operations.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Present results of and attendant recommendations from technology evaluations for appropriate command elements review/comment/concurrence.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Sunflower AAP Combined Waste Treatment Study

Intended User: Installation and service activity planning for activatio of production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Most currently inactive AAPs are not equipped with PEP production waste treatment facilities that would be required to meet today's regulatory requirements. Prior to operation and activation (except for an extreme national emergency), adequate waste treatment requirements would have to be established and systems designed and installed. Expedient measure could be taken to do so, but timing would preclude evaluation of alternative approaches that could result in significant waste treatment capital and operating costs.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1985-86 - Using Sunflower AAP as a representative PEP production installation, evaluate and determine best combined waste treatment for PEP production, acid plants and other attendant operations to minimize treatment capital and operational costs.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Provision of evaluation data package and attendant recommendations for use in activation plans.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Black Powder Production Sludge Treatment

Intended User: Black powder production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

New disposal technology is required for the waste filter cake resulting from the production of black powder. This waste has been tested and is indicated to be explosively reactive, and as such, cannot be delisted and must be disposed of as a reactive hazardous waste. Previous DA production of black powder occurred before current regulatory restraints were promulgated. Consequently, the previous practice of landfilling cannot be used. Open burning is another disposal alternative that may be possible as an expedient, but is not considered acceptable as a long-term disposal solution.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1985 - Filter cake characterization; engineering/economic evaluation of candidate treatment technologies and/or process changes.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Process changes and/or treatment system concept design recommended through command channels for implementation and operational testing in a black powder production facility.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: MMT Program Integration/Coordination

Intended User: AMC and Munition Production Base Modernization Agency

II. DEFICIENCY/NEED THAT TASK ADDRESSES

The Pollution Abatement and Environmental Control Technology (PACT) Program conducts research studies to develop and recommend technology to enable Army industrial facilities to achieve and maintain environmental compliance during their operation. The Manufacturing Methods and Technology programs seek to implement suitable technology for the same purpose by conducting more advanced development than that normally performed in the PAECT program. Each program has its separate function in achieving a common goal. Close coordination and integration of efforts are required for effective development of usable improved technology in the most cost-effective manner.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1985 - Establishment of a closer and more formal interfacing mechanism to assure necessary coordination of the two programs.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Recovery/Reuse of Explosives from Obsolete/Excess Munitions

Intended User: Defense Ammunition Directorate - DRSMC-DSM(R)

II. DEFICIENCY/NEED THAT TASK ADDRESSES

There are large stocks of unserviceable munitions now on hand, and this quantity increases annually as additional items are removed from the stockpile. The storage of these unserviceable munitions requires space and surveillance and costs money. Demilitarization of munitions via open burning or open detonation is also expensive and causes pollution which may not be acceptable to local and state regulatory authorities in the future. There is a need to determine if explosives from unserviceable munitions can be cost-effectively recovered.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1983-84 - Cost-effectiveness evaluation for the recovery and reuse of explosives.

FY 1985-87 - If determined to have adequate cost-effectiveness, determine the acceptability/requalification parameters in a laboratory study program (recovery methods and storage conditions).

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1984 - Publication and presentation of cost-effectiveness evaluation for appropriate command elements decision to further develop and implement the continual recovery/reuse concept.

FY 1987 - Preparation/transfer of a technical data package for conduct of advanced development studies of recovered explosive requalification for reuse.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Use of Energetic Wastes as Supplemental Fuel in Industrial Boilers

Intended User: Installation heating/power plants

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Obsolete and unuseable munitions containing explosives are currently destroyed by open burning/detonation. The use of these explosives as a supplemental fuel would significantly reduce fuel costs for industrial boilers at installations involved with obsolete/unserviceable munition disposal. Technical safety and economic feasibilty need to be evaluated in order to determine the benefit of implementing this supplemental fuel concept.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984 - Safety and cost-effectiveness evaluation; determination of normal fuel-energetic supplement mixing and delivery system concepts to be developed.

FT 84-85 - Determination of normal fuel-energetic supplement mixture combustion characteristics.

FY 1985-86 - Pilot plant studies.

FY 1987 - Large-scale demonstration.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1984 - Briefing of results of safety and cost-effectiveness evaluation to appropriate command elements; proposed further efforts for concurrence.

FY 1985 - Briefing of results of pilot studies to appropriate command elements; proposal of large-scale demonstration for concurrence.

FY 1987 - Presentation of results of large-scale demonstration to appropriate command elements along with provision of technical data package for adaptation of heating/power plants and implementation of this concept.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Reuse of Energetic Wastes as Supplemental Fuel in SSRP

Intended User: SSRP facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Energetic wastes exists at installations which will utilize the SSRP in TNT manufacture. Rather than simply destroying these wastes as a means of disposal, the potential exits for their use as a supplemental fuel for the multiple-hearth furnace used in the SSRP. This effort is being conducted to realize that potential which would result in operational cost as well as fuel savings.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Demonstration of technically feasible and safe methodology for reuse of selected energetic waste.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Preparation/transfer of technical data package for advanced pilot studies and full-scale demonstration/implementation.

I. TASK DESCRIPTION

Title: Off-Spec TNT Production Recycle Technology Development

Intended User: Continuous TNT production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Approximately 35,000 lb per month of off-spec TNT is currently generated per continuous production line. This material is incinerated. Incineration costs as well as product loss could be significantly reduced or eliminated if an effective means for recycle and requalification existed. TNT production operating personnel feel that recycle and requalification are feasible, but such a technology has not been developed.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1985-86 - Characterization of off-spec material; evaluation/selection of best recycle/requalification concepts; limited lab/pilot feasibility testing

FY 1986-87 - Support of actual implementation of demonstrated technologies; intense monitoring of operational parameters and results; lab/bench studies to supplement and confirm minor technology changes to correct problems encountered and/or optimize the technology.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Recommend recycle/requalification technology for implementation at an active production facility.

FY 1987 - Recommend operational/facility changes to accommodate recycle/requalification at all continuous TNT production facilities.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Propellant Reuse Technology Assessment

Intended User: Propellant production facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

If scrap, reject and/or surplus propellant are not reprocessed, they must be disposed of in compliance with regulatory requirements. Currently, the disposal technology applied is incineration. Reprocessing has been performed only on a limited basis because of high costs and safety hazards inherent in existing reprocessing technology. The cost-benefit of reprocessing propellants on a significantly large scale has not been clearly defined, but is suspected to be such that an investment in development of improved technology would result in a substantial payoff.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1985 - Determine cost-benefit of developing improved propellant reprocessing technology.

FY 1986 - Assuming reprocessing technology development is determined to be cost beneficial, technology alternative concepts will be evaluated or selected for experimental development.

FY 1987 - Lab/bench studies to develop selected improved technology concepts.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Publication/distribution of cost-benefit analysis and results along with recommended further development efforts.

FY 1987 - Preparation/transfer of exploratory development technical data package for advanced development efforts.

I. TASK DESCRIPTION

Title: PEP Incineration Heat Recovery

Intended User: PEP incineration facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Ammunition plants, depot activities, and depots that currently operate PEP incinerators (or are constructing same) have not included provisions for heat recovery. The cost-benefit of heat recovery/reuse has not been addressed in any depth. There is a need to determine the cost-benefit of employing different technically feasible heat recovery alternatives because of the potential fuel savings and operational cost reductions involved.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1986 - Determination of cost-benefit of technically feasible heat recovery alternatives.

FY 1987 - Bench-scale development (if cost-beneficial).

FY 1988 - Large-scale demonstration.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Recommendation for employment of heat recovery based on cost-benefit evaluation.

FY 1988 - Provision of technical data package for facility adaptation concept design to implement recommended heat recovery technologies.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Degreaser Wastes Recovery/Reuse Technology

Intended User: Degreasing facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Because of changes in the extent and nature of degreasing operations as well as applicable environmental regulations, the need for improved degreaser wastes disposal and/or recovery/reuse technology should be assessed periodically. Such an assessment was made in FY 1981. Results at that time indicated that an improved technology development program was not warranted due to the low potential for significant disposal and/or reuse recovery cost reductions.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1986-87 - Conduct of current technology assessment for disposal and reuse/recovery of degreasing wastes.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1987 - Recommended technology development based on results of assessment.

I. TASK DESCRIPTION

Title: Paint Reformulation

Intended User: Manufacturing and material maintenance facilities involved with paint application

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Prior to the promulgation of volatile organic compound (VOC) air pollution emission regulations, paint formulation state-of-the-art generally involved using high solvent or VOC concentrations. In order to comply with regulations and minimize or eliminate the need for air pollution controls in painting operations, reformulation of paints required to eliminate or significantly reduce the quantities of VOCs that they contain.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1980-84 - Conduct the reformulation and product testing studies to reduce/eliminate VOC content of paints used for military applications.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1980-85 - Revisions of military specs for procurement of paints in DA.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Electroplating Waste Sludge Treatment Technology Development

Intended User: AMC plating and metal finishing facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

More cost-effective technology is required for the disposal of sludges. Current practice consists of contracted hazardous waste landfill disposal at costs reportedly ranging from $90 to $300 per drum. These costs are anticipated to increase in the future as landfill space becomes scarcer.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Determination of delisting requirements/possibilities, and justification for development of improved technology based upon assessment of state-of-the-art processes and cost-benefit analyses.

FY 1985-86 - Lab/bench scale study of treatment processes justified for development as improved technologies. (Direction of this effort, and possibly termination, will be dependent on the results of the sulfide precipitation process economic evaluation.)

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Presentation of delisting guidelines to users, and presentation of improved technology development justification bases for review/concurrence by appropriate command elements.

FY 1986 - Preparation/transfer of technical data package for advanced development pilot plant studies.

I. TASK DESCRIPTION

Title: Sulfide Precipitation Process Pilot Study

Intended User: AMC electroplating facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Sulfide precipitation treatment for plating wastewaters has been found to produce a sludge that is more effectively dewatered and exhibits lower metal ion leachability than the currently used hydroxide precipitation process sludge. Metal ion leachability has, in some cases, been so low that delisting of the sludge as a hazardous waste has been possible, thereby eliminating hazardous waste disposal costs. If the sludge is classified as hazardous despite lower metal ion leachability, the sulfide precipitation process still may be more cost-effective due to the fact that more efficient dewatering results in a lesser volume of sludge to be disposed of in a hazardous waste facility.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984 - Complete design, installation and initial operation of a prototype sulfide precipitation system at Tobyhanna Army Depot.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Employment of performance data for comparison with other new alternate treatment technologies; preparation of technical data package for adaptation and installation at other AMC plating waste treatment facilities.

POLLUTION ABATEMENT AND ENVIRONMENTAL CONTROL TECHNOLOGY

I. TASK DESCRIPTION

Title: Economic Evaluation of the Sulfide Precipitation Process

Intended User: AMC plating and metal finishing facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Sulfide precipitation treatment for plating wastewaters has been found to produce a sludge that is more effectively dewatered and exhibits lower metal ion leachability than the currently used hydroxide precipitation process sludge. Metal ion leachability has, in some cases, been so low that delisting of the sludge as a hazardous waste has been possible, thereby eliminating hazardous waste disposal costs. If the sludge is classified as hazardous despite lower metal ion leachability, the sulfide precipitation process still may be more cost-effective due to the fact that more efficient dewatering results in a lesser volume of sludge to be disposed of in a hazardous waste facility. These indicated cost savings must be verified by detailed economic analysis before seriously considering adaptation of the process at facilities.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Economic evaluation of implementation of the sulfide precipitation process at representative AMC plating facilities.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1985 - Presentation of detailed economic evaluation to appropriate command elements along with attendant recommendations.

I. TASK DESCRIPTION

Title: Paint Sludge Disposal Technology

Intended User: Depot and ammunition plant paint application and stripping facilities

II. DEFICIENCY/NEED THAT TASK ADDRESSES

Sludges generated in the applications as well as stripping of paint during manufacturing and material maintenance operations are regulated as hazardous wastes. The current means of disposal, contracted hazardous waste landfilling, is projected to continue to become more costly as proper landfill area becomes scarcer. More cost-effective technology should be made available.

III. TECHNOLOGY DEVELOPMENT PLAN

FY 1984-85 - Evaluation of disposal technology alternatives; selection of best alternatives for development.

Fy 1985-86 - Lab/bench scale development of selected alternative concepts.

IV. PLANS FOR TECHNOLOGY TRANSFER/IMPLEMENTATION

FY 1986 - Preparation/transfer of technical data package for advanced development pilot plant studies.

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